

PROCESSES AND PROPERTIES INDEX

Synthesis of alcamino acids by the cyanohydrin method. A. I. KIPRYASOV AND G. I. KIPRYANOV. *J. Gen. Chem.* (U.S.S.R.) 2, 585 (1942). The proposed term "alcamino acid" is constructed from alcamine (amino alk.) and amino acid to distinguish this type of aminohydroxy acids from that of α -amino. In the synthesis of alcamino acids

by the interaction of α -hydroxy acids and amino acid esters is usually obtained a mixt. of monohydroxyalkyl and dihydroxyalkylamino acids, the separ. of which is very difficult, and in the lower amino acids, such as glycocyl and alanine, is impossible (c. 1, 21, 210, 22, 3134, 36, 100). Zelinskii and Stadnikov (*J. Russ. Phys. Chem. Soc.* 38, 722, 40, 700) produced amino acids from CO compds. with KCN and NH_3 , while by using amines in place of NH_3 can be obtained amino acids substituted in the NH_2 group. It was found that by using amino alcs. instead of NH_3 with CO compds. and KCN are easily obtained good yields of alcamino nitriles which on sapon. give alcamino acids. Thus the HCl salt of ethanodamine (I), condensed at room temp. with CH_3CO , Me_2CO , EtOH and cyclohexanone (II), produced with liberation of heat 70% of alcamino acids synthesized for the 1st time. I condensed with II gave *hydroxyethylamino cyclohexanone nitrile*, $\text{C}_6\text{H}_{11}(\text{CN})\text{NH}(\text{CH}_2)_2\text{OH}$ (III), which on sapon. produced *hydroxyethylamino cyclohexanone carboxylic acid*, $\text{C}_6\text{H}_{11}(\text{CO}_2\text{H})\text{NH}(\text{CH}_2)_2\text{OH}$ (IV). In other cases the nitriles were not sapon. but directly saponated to the acids. EtOH gave with I *phenylhydroxyethylaminosuccinic acid*, $\text{C}_6\text{H}_5\text{CH}(\text{CO}_2\text{H})\text{NH}(\text{CH}_2)_2\text{OH}$ (V), Me_2CO , *dimethylhydroxyethylaminosuccinic acid*, $\text{Me}_2\text{C}(\text{CO}_2\text{H})\text{NH}(\text{CH}_2)_2\text{OH}$ (VI), and CH_3CO , *hydroxyethylaminosuccinic acid*, $\text{CH}_3(\text{CO}_2\text{H})\text{NH}(\text{CH}_2)_2\text{OH}$ (VII). I, b. 170-2°, was prepd. by Knorr's method (Ger. pat. 97,102) and converted to the HCl salt with concd. HCl to neutral reaction to litmus, and used in soln. (48 g. in 100 cc.). V was prepd. when a mixt. of 3.3 g. KCN in 15 cc. H_2O , 5.1 g. EtOH , 10.5 cc. LiHCl and 15 cc. MeOH was digested 15 days, the MeOH distd. off, the oil extd. with Et_2O , the Et_2O expelled, the oil dissolved in dil. HCl, any insol. matter extd. with Et_2O , then concd. by evapp., sapond. with concd. HCl, after 2 hrs. standing chld. with H_2O , concd. on the water bath, sapon. from NH_4Cl by treating with alc. and

Et₂O, there was obtained 8.4 g. (71.8%) of V; HCl salt in 1.5 ml in a sealed capillary tube (decomprn), sol. in H₂O and alc. About 65% of the free acid of V was sepd. by treating a concd. soln. of the salt with concd. NH₃ to neutral reaction, and the rest by the Ag(OH)₂ and H₂S method. V, m. 217.8° in a sealed capillary tube, is poorly sol. in cold H₂O and alc., insol. in Et₂O. A yield of 7.25 g. (61.8%) of III, m. 78.8°, was prepd. when a mixt. of 30 cc. soln. of 1.8 g. KCN, 12 g. H₂O, 1.5 ml. Et₂O, and 50 cc. Et₂O was digested 1 day, the ether layer sepd., the aq. layer extd. with Et₂O, the combined ether exts. dried with K₂CO₃, the Et₂O expelled, white crystals from Et₂O, easily sol. in alc., sparingly sol. in H₂O. The HCl salt of III, m. 95.8°, was prepd. by passing dry HCl into III in Et₂O. The aq. layer of the reaction and the mother liquor from the sepn. of III were combined and hydrolyzed with HCl, the reaction mass was evaporated to dryness, the mineral salts were sepd. by recrystg. from alc. IV was sepd. from its HCl salt with NH₃, and the mother liquor subjected to similar operations produced in all 10 g. (41.9%) IV, (41.9%), or 75.7% of III and IV combined. IV, m. 252.4° in a sealed capillary tube, is sol. in H₂O, poorly sol. in alc., and insol. in Et₂O. VI was obtained in 6 g. yield (40%) by digesting 1 day a mixt. of 0.75 g. HCl salt of I, 0.5 g. KCN, 5.8 g. Me₂CO and 25 cc. H₂O, hydrolyzing with an equal vol. of concd. HCl on the water bath for 2 hrs. and sepg. the mineral salts as above. The sepn. of a cryst. HCl salt of VI being impossible, the free acid was obtained by the Ag(OH)₂ method. VI, m. 240.5° in a sealed capillary tube, is sol. in H₂O, little sol. in alc., and insol. in Et₂O. VII, m. 174.5°, was obtained in 5.7 g. yield (62.5%) when a soln. of 5 g. KCN was added dropwise in 3 hrs. with stirring and cooling to a mixt. of 5.7 g. HCl salt of I and 5.8 g. 40% CH₃CO, and allowed to stand 1.5 hr. at room temp., an equal vol. of concd. HCl was added, let stand 12 hrs., digested 1.5 hrs. in a water bath, sepd. from KCl and NH₄Cl and worked up with Ag(OH)₂ as above; white crystals were obtained easily sol. in H₂O, slightly sol. in alc., and insol. in Et₂O.

CHAS. H. BANC

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Use of polychlorobenzenes in the synthesis of dyes. III. Preparation of *p*-chlorophenol from *p*-dichlorobenzene. A. I. KIPRIYANOV AND M. M. DABEYEVSKI. *Ukrain. Khim. Zhur.* 7, Wilm.-tech. Abt. 78-80(1972), cf. C. A. 25, 5884.—The hydrolysis of $p\text{-C}_6\text{H}_4\text{Cl}_2$ with aq. NaOH gives a max. yield of 30% of $p\text{-C}_6\text{H}_4\text{ClOH}$ (I); 2.5 mols. of alkali suffice for the complete removal of Cl. With NaOH-MeOH and a little Cu powder at 225° yields up to 85% are obtained, probably because of the inactivity of the $\text{C}_6\text{H}_4\text{ClONa}$ formed in the medium. IV. Preparation of *p*-aminophenol from *p*-dichlorobenzene. A. I. KIPRIYANOV, G. I. KIPRIYANOV AND M. M. DABEYEVSKI. *Ibid.* 87-89.—The influence of various factors on the formation of $p\text{-H}_2\text{NC}_6\text{H}_4\text{OH}$ from (I) and aq. NH_3 in presence of CuSO_4 has been examined. The optimum yield (82.5%) was obtained by heating with 4 vols. of 33% NH_3 and 16% of CuSO_4 for 2 hrs. at 165°. V. Preparation of pyrocatechol from polychlorobenzenes. A. I. KIPRIYANOV AND R. D. SUTCH. *Ibid.* 94-100.— $o\text{-C}_6\text{H}_4\text{Cl}_2$ is hydrolyzed to $o\text{-C}_6\text{H}_4\text{ClOH}$ with 2.5 mols. of NaOH-MeOH at 225° in a rocking autoclave. The further hydrolysis to pyrocatechol by NaOH in presence of CuSO_4 gives yields up to 71%, provided a Cu- or Ag-lined autoclave is employed. $\text{Na}(\text{OH})_2$ and Na_2CO_3 are unsatisfactory hydrolytic agents. The concn. of alkali must not exceed 10%, but the temp. and duration of heating are of secondary importance. B. C. A.

ASH-51A METALLURGICAL LITERATURE CLASSIFICATION

Co

Determination of β -naphthalenesulfonic acid. A. I. Kiprenov, N. M. Nikolavskii and E. A. Bilenko. *Zavodsk. Lab.* 3, 414 (1934). The detn. of β -C₁₀H₇SO₃Na (I) and indirectly of α -C₁₀H₇SO₃Na (II) in a sulfonation mixt. is based on the insoly. of β -C₁₀H₇SO₃Na (III) and the soly. of α -C₁₀H₇SO₃Na in a concd. soln. of MgCl₂ or MgSO₄. The method gives sufficiently accurate results for the control of sulfonation of C₁₀H₈ in the production of β -C₁₀H₇SO₃Na with a considerable saving in time and labor as compared with the procedure of Finner (J. I. S., 2702). By pptg. III from a concd. soln. of 0.5-1 g. of the mixed acids with 80 cc. of 40% MgCl₂, washing the ppt. with 35% MgCl₂ and detg. S by the Fehle method, the values obtained are 1% low; this is probably caused by a partial hydrolysis of III by washing and is confirmed by somewhat high values for H₂SO₄ in the sulfonation mixt. The use of the time-consuming Fehle method can be avoided by substituting MgSO₄ for MgCl₂ as a precipitant. MgSO₄·7H₂O heated at 135° gives the stable hydrate MgSO₄·H₂O without the formation of a basic salt. Hence by drying a mixt. of MgSO₄ and III at 135° to a const. wt. and then detg. the sulfate ion, the percentage of MgSO₄·H₂O and that of III by difference can be calcd. Dissolve 7.5 g.

of the sulfonation mixt. in 100 cc. H₂O, filter, wash and weigh the insol. residue, dil. the filtrate to 200 cc., withdraw 50 cc. of the soln., add 2-3 cc. of methyl red soln., neutralize on a water bath with dry MgO, dissolve any excess of MgO with a few drops of dil. H₂SO₄, add, with stirring, hot acid. MgSO₄ (30 g. MgSO₄·7H₂O in 10 cc. H₂O), digest 1 hr. in a boiling-water bath, let stand overnight at room temp., filter off the ppt. through a dried and weighed 2-hd. crucible with a porous bottom with strong suction (do not wash the ppt.), use the filtrate for transferring the ppt. from the beaker to the filter, dry the crucible with the ppt. 2-3 hrs. at 100° and 3-4 hrs. at exactly 123.5° to a const. wt. and weigh, dissolve the ppt. in hot H₂O, dil. to 50 cc., acidify with HCl, det. S by BaCl₂, and calc. the percentage of MgSO₄·H₂O and that of III by difference. H₂SO₄ in the sulfonation mixt. is detd. with BaCl₂ in a sep. sample. II is detd. indirectly by titrating the total acidity with 0.1 N NaOH against methyl red and then calc. The results of 10 cetns. of the same sulfonation mixt. are: I 50, 50.6, 50.6, 50.8, 50.9, 50.9, 50.9, 50.9, 50.9, mean 50.7%, and II (calcd.) 17.4%. The accuracy, checked with an artificial mixt. of recrystd. Kahlbaum I and II, is 0.3-0.7% (high). The same sulfonation mixt. detd. by pptn. with MgCl₂ and detn. of S by the Fehle method gave from 50.8 to 50.8%, I with an av. of 50.4%. C. H.

438-35.8 METALLURGICAL LITERATURE CLASSIFICATION

CPA

Determination of benzene-mono- and -disulfonic acids
A. I. Kipyryanov and E. D. Suchk. *Zashchita Laz. 3, 1023-84 (1964)*—Three g. of material is dissolved in 250 cc. of H_2O , H_2SO_4 is added in 25 cc., and total acidity in a second 25-cc. portion by titration with 0.1 N KOH (phenolphthalein). The titrated soln is evaporated to dryness, and the residue of K salts is heated at 250° to const. wt. The percentage content of $NaHSO_4$ is $135.15(A - 0.0157A_1)$, and of $CaHSO_4$ is $141.80(0.0104A - S_1)$, where S_1 is the wt. of K salts less that of K_2SO_4 , and A is total acidity less that due to H_2SO_4 . B. C. A.

A 10 1 L A METALLURGICAL LITERATURE CLASSIFICATION

| PROCESSING AND PROPERTY INDEX | | | | | | | | | |
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| <div style="display: flex; justify-content: space-between;"> ca 10 </div> | | | | | | | | | |
| <p> Oxidation of acenaphthene to acenaphthenequinone. A. I. Klorinov and M. M. Tushrevskii. <i>J. Appl. Chem.</i> (U. S. S. R.) 7, 944 (1954). In the oxidation of the acenaphthene to acenaphthenequinone a considerable residue is obtained, insol. in Na_2CO_3 and NaHSO_4, which lowers the yield of the acenaphthenequinone. This residue is composed of an isomeric mixt. of acenaphthenequinone and naphthalic acid anhydride. The low sol. of the latter in Na_2CO_3 and NaHSO_4 is probably due to the difference in the chem. properties of the consecutive mol. layers of the crystal structure. The isomeric mixt. may be sep. by exg. with Na_2CO_3 and NaHSO_4 at elevated temps. and pressures or by treating the mixt. in hot PhNO_2 with the same substances; this raises the small yields of acenaphthenequinone. A. A. Bochtlingk </p> | | | | | | | | | |
| ASD-5LA METALLURGICAL LITERATURE CLASSIFICATION | | | | | | | | | |
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/ Amino-acids (hydroxyalkanoic-acids);
their synthesis and reactions. A. I. KIRMANOV
(Trav. Inst. Chim. Charkov, 1955, 1, 26-51). A
review of published papers. In: R. T.

ASB SLA DETAILING LITERATURE CLASSIFICATION

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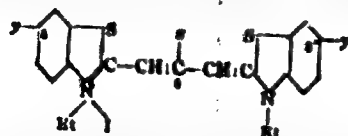
| PROCEDURE AND PROPERTIES | |
|--|---|
| <p>(A) Cyanine dyes from amino-derivatives of benzothiazole. (B) Cyanine dyes from isomeric dimethylbenzothiazoles. A. I. Kuvshinov and M. D. Siroch (Trav. Inst. Chim. Charkov, 1948, 2, 15-24, 25-37). (A) 5-Dimethylamino-1-methylbenzothiazole, m.p. 71°, prepared from 5-amino-1-methylbenzothiazole and p-O, N, M, O, M, or by a Stobbe synthesis from MPh₃, yields a compound 5-N-(I) and a colorless 5-N-methiodide, both m.p. 202° (decomp.), and a 5-N-(II), m.p. 243°, and 5-N-ethiodide, m.p. 166°; the yield of 5-N-derivative rises with increasing duration and temp. of reaction with the alkyl iodide. 5-Dimethylamino-1-methylbenzothiazole, b.p. 185-190°/16 mm. (5-N-ethiodide (III)), m.p. 76°, was prepared analogously. In picoline (at the b.p.) $CH_3(OEt)_2$ and (I), or (II) yield 3:5'-bis(dimethylamino)-5:2'-dimethyl- (IV), m.p. 244°, or 3:5'-bis(dimethylamino)-5:2'-bisethiocyanatopyrene iodide (V), and 3:5'-bis(dimethylamino)-5:2'-bisethiocyanatopyrene iodide (VI) is prepared similarly from (III). The 8-Me derivative of (IV) is obtained when NMe_3 is added to the reaction mixture. The 8-Me derivatives of (V) and (VI) are prepared similarly to them, using $CH_3(OEt)_2$ in place of $CH_3(OEt)_2$.</p> | <p>2-Isodequinoline ethiodide and (I) in $KOH-KOH$ (1 hr. at the b.p.) yield 5-dimethylamino-1-methyl-3'-ethyl-3'-isodequinoline iodide, m.p. 171°, whilst with quinoline methiodide 5-dimethylamino-1':2'-dimethylthiocyanatopyrene iodide, m.p. 176°, is obtained. Max. light absorption data are recorded for the above dyes. The dyes are valuable constituents of photographic emulsions.</p> <p>(B) Thiocet-toluidide in aq. NaOH and aq. K_2CO_3 at 7° yield 1:3-dimethylbenzothiazole, b.p. 161-163°/25 mm., the ethiodide, m.p. 150°, of which give: 3:5'-dimethyl- or 3:3':5-trimethyl-2:2'-bisethiocyanatopyrene iodide when heated with $CH_3(OEt)_2$ or $CH_3(OEt)_2$, respectively. 2-Amino-4-methylthiophenol and Ag_2O in CH_2 (at the b.p.; 2 hr.) yield 1:4-dimethylbenzothiazole, b.p. 153-156°/25 mm., m.p. 84°, from the ethiodide, m.p. 195-196°, of which are prepared 4:4'-dimethyl- and 4:4':8-trimethyl-2:2'-bisethiocyanatopyrene iodide. The sensitizing action of the isomeric dyes is unaffected by position of the Me, but the greatest bathochromic effect is given by the 4:4'-Me₂ derivatives. R. T.</p> |

25

Influence of the anion on the properties of thiocyanine dyes. A. I. Kiprakov and R. Shuser. *Proc. Charkov State Univ.* 4, 49-53(1936). By condensing CMe(OEt)₂ or CH(OEt)₂ with the appropriate thianole alkiodides, etc., 8-methyl-2,2'-diethylthiocarbonyl chloride, bromide, m. 243°, and iodide, 5,5',8-trimethyl-2,2'-diethylthiocarbonyl bromide, m. 240°, and iodide, and 2,2'-diethyl-3,6,3',6'-dibenzithiocarbonyl chloride, m. 190°, bromide, m. 281°, and iodide were prepd. The anion of the dye scarcely affects its sensitizing properties.

B. C. A.

Cyanine dyes. I. Thionin derivatives. A. I. Kishner, J. P. Saitnik and R. D. Saitnik. *J. Gen. Chem.* (U.S.S.R.) 6, 42-9 (1956).—Kilven dyes of the general formula



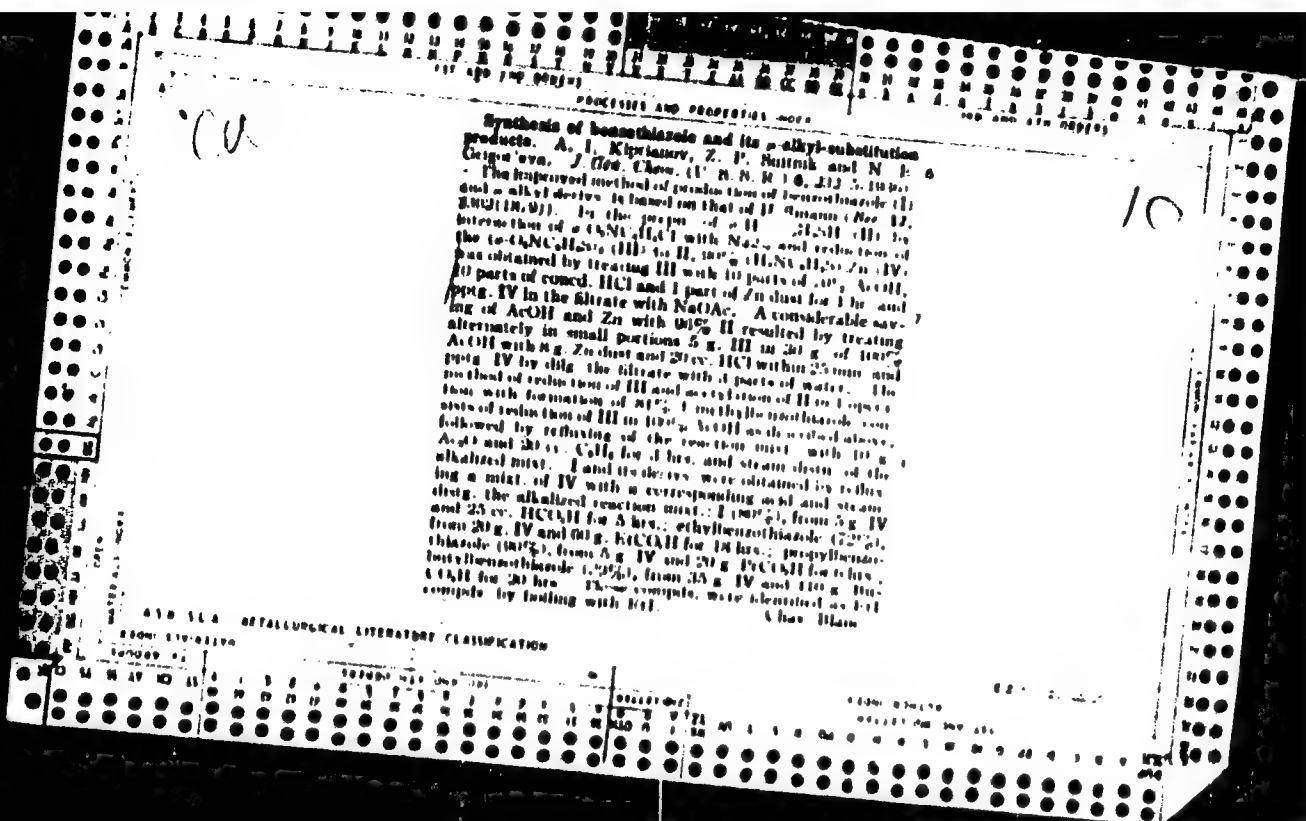
were synthesized in which x is H, Me, OMe or Ph and y is H, Me or ORt. Attempts to prep. the 8-Ph and 8,8'-di-8-O derivatives were unsuccessful. The general synthetic method used was condensation of the quaternary salts of the heterocyclic bases containing a reactive Me group with esters of ortho acids. All 8-benzothiazines were prep. by Jacobson's method which consists in fusing the Ac. derivs. of the aromatic amines with P_2S_5 and oxidation of the resulting thioamides with $K_2Fe(CN)_6$. The yield of thioamides has been increased from 50 to 80-90% by introducing better control of the fusion temp. Unpurified P_2S_5 was used. Thiophenacetin m. 117° (from AcOH) (according to Sachs and Lowry, m. 99-100°; cf. Ber. 37, 276). A new compd., 1-methyl-4-ethoxybenzothiazole (I), m. 57.5°. Increased yields of some of the esters are reported: $HC(OEt)_2$, 45%; $MeC(OEt)_2$, 60% (cf. Ber. 13, 116; C. A. 32, 343). The max. absorption observed in alc. for $y = H$, Me and ORt , temp., are as follows: $x = H$,

8480, 8480, 8710; Me, 8330, 8430, 8540; OMe, 8660, 8430, 8640; Ph, 8600. —. Substituents in the 8-position, regardless of their nature, increase the sensitizing action of the thionin derivatives. A finely divided mixt. of 33 g. P_2S_5 and 54 g. $PhNHAc$ was heated on a water bath with continuous stirring until the whole mass was molten and then for 5 min. more. Estn. of the cooled melt with successive portions of 8% aq. NaOH until the alk. est. no longer was rendered turbid by acidification, added of 48. H_2O , to the remainder est. in separate pptn. and pptn. with CH_3 gave 61.6% of impure thionin derivative, m. 78-80°, suitable for the prep. of 1-methylbenzothiazole (II). P_2S_5 was prep. by melting together F and S in theoretical proportions. p -Thionin derivative was prep. by an analogous method at 130° in 55% yield. Thiophenacetin, 30% yield, m. 113-14°. The yields of benzothiazines and their ethiodides were: II, m. 125°, 50% ethiodide, m. 191°, 90%. 1,5-dimethylbenzothiazole (III), diid. in vacuo, 50%; ethiodide, m. 156-70°, 84%. I, m. 57.5° (from alc.), m. 135-40°, 25%; ethiodide, m. 161-2° (from alc.), 85%. In the prep. of $HC(OEt)_2$, the higher yield is obtained by adding the $CHCl_3$ to a gently boiling

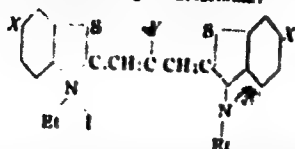
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[α]_D -87.3° was prepd. by cong. 15 g. V in 150 cc. MeOH with dry NH₃ at 0° and letting it stand at room temp. for 24 hrs. After cong. the mixt. in vacuo, the syrup was distd. at 118° and reduced pressure until it was freed from AcNH₃. Choral. digested with a large excess of MeI and AgOAc for 20 hrs. gave 2,4,6-trimethylglucal, [α]_D 31.4°. This (10 g.) in 10 cc. CHCl₃, treated with Cl at 0° and the CHCl₃ distd. off in vacuo, gave 9.1 g. 1,2-dichloro-3-trimethylglucal, [α]_D 131.1° (CHCl₃). This in CHCl₃, shaken with conc. AgI, gave III. III in H₂O, heated gently with Pb(OH)₂, gave 60% IV; its phenylhydrazide m. 22-5°. IV was converted with EtI into VIII and this into IX.

Chas. R. Rane



Relation between the structure and optical and photographic properties of cyanine dyes. II. Thiocyanines with substituents containing sulfur. A. I. Kiprianov, Z. P. Saitnikov and R. D. Murzh. *J. Gen. Chem. (U. S. S. R.)* 6, 576 (1936); (*J. C. A.* 30, 4969, 4952). The function of S in the thiocyanine dyes in producing the sensitizing and stabilizing properties was studied by synthesizing and testing thiocyanine derivs. contg. S in the substituents in addn. to the S in the heterocycles. Five dyes were produced of the general formula:



where X and Y are substituents contg. S (a thioalkyl or the simplest group). The results show that S substituents have no effect on the sensitizing and stabilizing properties of thiocyanine dyes. In the synthesis of the dyes several new methods and compounds were developed and identified. A diazo salt from 8.2 g. amino-1-methylbenzothiazole, m. 122° (Sheppard, *Ind. soc. franc. phot.* 12, 382 (1925)), and 3.5 g. NaNO_2 is treated with 13 g. of cryst. NaOAc and then poured, with stirring, into 10 g. K santhate in 50 cc. H_2O at 70°. The oily santhate is extd. with Et_2O and, after drying and freeing from the Et_2O , it is boiled with 8 g. KOH in 50 cc. alc. for 3 hrs. the alc. is distd. off and the residue is shaken with 5.2 g. Me_2SO in 100 cc. H_2O , giving 6.1 g. methyl-1-methyl-

benzothiazole (I). EtI deriv. (II), m. 215°, resulted in 2.3 g. yield from 5.1 g. I and 5 g. EtI by heating the mixt. in a sealed tube at 100° for 4 hrs. II (0.9 g.) with 0.8 g. HC(OEt) , in 5 g. of dry $\text{C}_2\text{H}_5\text{N}$ is digested in an oil bath for 3 hrs., giving 75% dye, 2,2'-dimethyl-5,5'-methylmercaptobenzothiazolopyranine iodide. II (0.4 g.) and 0.4 g. MeC(OEt) , in 3 g. $\text{C}_2\text{H}_5\text{N}$ heated for 1.5 hrs. gave 30% 2,2'-dimethyl-5,5'-dimethylmercaptobenzothiazolopyranine iodide. MeSH is obtained in 80% yield when a NaSH soln. (from 100 g. NaOH in 600 cc. H_2O extd. with H_2S) is slowly treated, with stirring, with 125 g. Me_2SO (1 hr.) under a condenser cooled with ice and water. Me_2SO , b. 38°, is retained in the reaction flask, while gaseous MeSH is conducted through a CaCl_2 U-tube and is condensed by a freezing mixt. EtSH , b. 37°, is similarly prepd. in 70% yield with the condenser fed with H_2O at 40-50°, retaining Et_2S , b. 92°, in the flask. MeSCH_2CN , b. 74.5°, resulted in 50% yield when a soln. of 37.5 g. MeSH with 18 g. Na in 230 cc. of abs. alc. was slowly introduced, with stirring, into 50 g. $\text{C}_2\text{H}_5\text{CN}$ in alc. The filtrate from NaCl was freed from the alc. and the residue redistd. $\text{MeSCH}_2\text{CO}_2\text{Et}$, 174.6°, is prepd. in 31.6% yield from an equimol. mixt. of $\text{C}_2\text{H}_5\text{CO}_2\text{Et}$ and MeSCH_2CN in alc. by dilg. it with H_2O and redistg. the oil. A mixt. of 24 g. of the ester with 61 g. of 22% NH_4OH after standing for 24 hrs. gave 67.5% $\text{MeSCH}_2\text{CONH}_2$, b. 104°. $\text{MeSCH}_2\text{C(NH)OEt}$ (III) is prepd. in 85.5% yield by conducting 10 g. of dry HCl into 22.5 g. MeSCH_2CN in 15 cc. of abs. alc. After 4.5 hrs. III HCl is filtered off and decumped. with KOH. $\text{MeSCH}_2\text{C(OEt)}$ (IV),

by 78-80°, resulted in 25% yield from 10 g. III. HCl in 15 cc. of abs. alc. after standing for 7 days. The diarsite from NH_4Cl is freed from the alc. and the residue redissolved. $\text{K}_2\text{S}(\text{H}_2\text{N})_2$ by 104-5° (89.5% yield) (16 g.) in 7.2 g. alc. treated with 7 g. HCl at -15° gave 80% $\text{K}_2\text{S}(\text{H}_2\text{N})_2$ (I: NINON) (V), by 103-4°. 3,3'-Diethyl-5-methylmercaptomethylthiocarbonyl diarsite resulted in 34% yield from 1-methylthiomethanols-1:1 (VI) and 3.9 g. III in 10 cc. of abs. alc. by heating 1 hr. The same dye is obtained from VI and IV in 23% yield. 3,3'-Diethyl-5-methylmercaptomethylthiocarbonyl diarsite (11% yield) resulted from 3 g. VI and 5.1 g. V. 3,3'-Diethyl-5,5'-dimethyl-5-methylmercaptomethylthiocarbonyl diarsite (11% yield)

is prepd. from IV and 1,5-dimethylthiomethanols (Bernth & Ann. 231, 111 (1899)).
Chas. H. H. H.

Reaction of ethanalamine with aldehydes and malonic acid. A. I. Kiprianov and T. S. Kuznetz. *J. Gen. Chem.* (U. S. S. R.) 6, 841-4 (1936).—Previously it was shown that the condensation of $\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$ (I) with aldehydes or ketones and HCN results in alkanino acids (C. A. 27, 1618). Rodionov (C. A. 21, 1257; 21, 1882) has shown that the condensation of aldehydes with NH_3 and $\text{CH}_3\text{CO}_2\text{H}$ (II) gives good yield of β -amino acids, and that the substitution of EtNH_2 for NH_3 gives poor results. Attempts to synthesize alkanino acids by this reaction by substituting I for NH_3 and alkanamines gave neg. results. Refluxing 8 g. EtNH_2 , 9 g. II and 6.1 g. I in 80 cc. alc. on a water bath for 6 hrs. gave 81% cinnamic acid (III) and no amino acids. A similar mixt., obtained by refluxing with water, was allowed to stand overnight at room temp., giving 83% $\text{PhCH}:\text{C}(\text{CO}_2\text{H})_2\text{H}_2\text{N}(\text{CH}_2)_2\text{OH}$ (IV), m. 135-6° (decomp.), and not $\text{PhCH}(\text{NHCH}_2\text{CH}_2\text{OH})\text{CH}(\text{CO}_2\text{H})_2$, according to the Rodionov reaction of condensation with NH_3 or an amine. Under these conditions fur-

fural gave 78.5% $\text{O}:\text{CH}:\text{CH}:\text{CH}:\text{CCH}(\text{CO}_2\text{H})_2\text{NH}_2$ (V), m. 127° (decomp.); salicylaldehyde gave 79% of the salt of coumarinacetic acid (VI), m. 108-79° (decomp.), and piperonal 84% of a corresponding 7° (decomp.), which could not be recrystd. These compounds, which could not be recrystd. These compounds are not β -aminocoumarinacetic acids because on heating they cleave CO_2 .

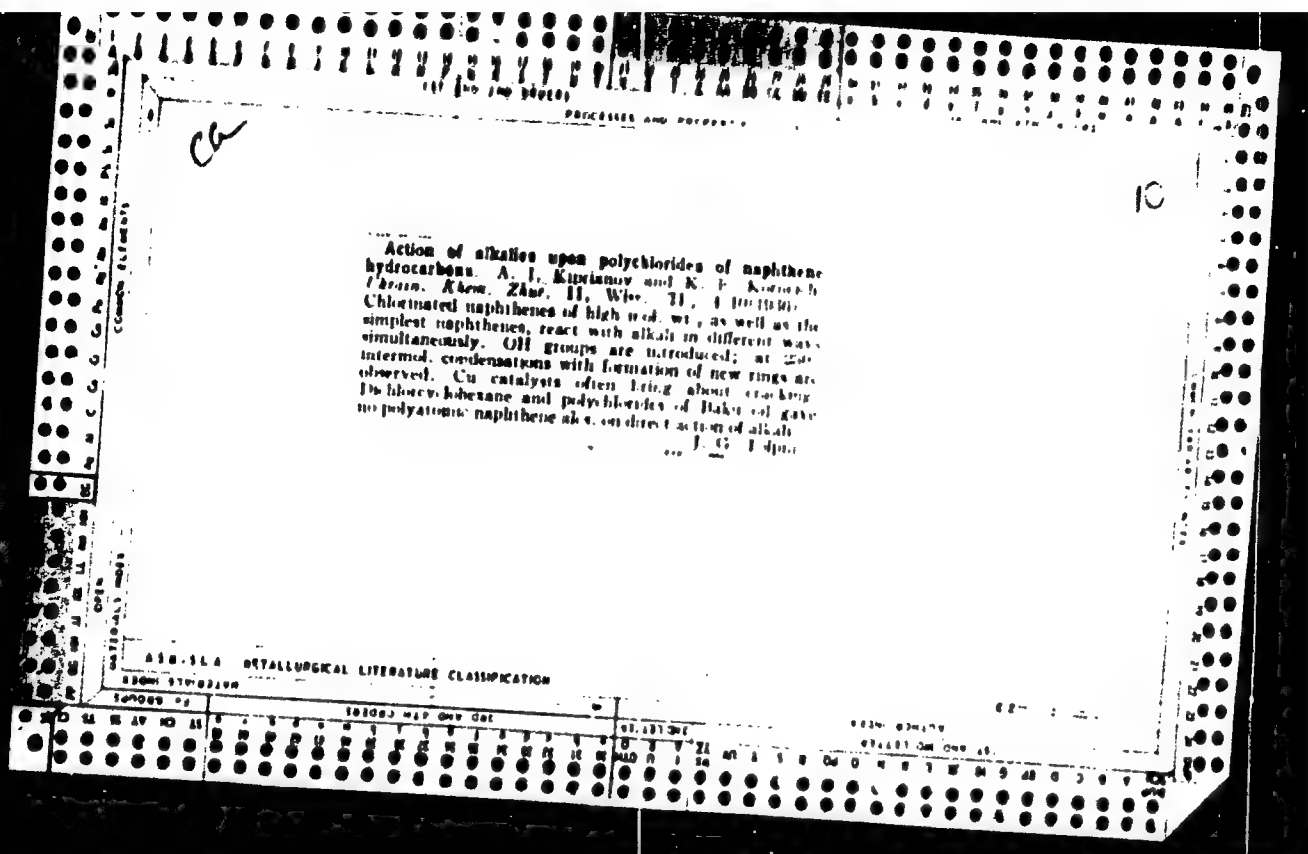
and I, giving the derivs. of III. Thus IV on heating gave III, and by decarbox. in H_2O with dil. H_2SO_4 there resulted 76% $\text{PhCH}:\text{C}(\text{CO}_2\text{H})_2$, m. 193° (decomp.) (cf. Knoevenagel, *Ber.* 31, 2704 (1908)). V with dil. HCl gave 96% $\text{O}:\text{CH}:\text{CH}:\text{CH}:\text{CCH}:\text{C}(\text{CO}_2\text{H})_2$, m. 197° (decomp.) (Knoevenagel, *loc. cit.*). VI with dil. HCl gave 91% coumarinacetic acid, m. 187-8° (cf. Stuart, *J. Chem. Soc.* 49, 358 (1926)). On the addn. of equimol. amts. of I and II, and its derivs. in alc. there are formed compounds identical with the condensation products of I with aldehydes and II.

Mercurial derivatives of α -crotonic acid. A. Lempagnol and D. Bar. *Bull. soc. chim.* [5], 3, 1107-14 (1908).—By an application to the study of the Hg derivs. of α -crotonic acid of the methods used to establish the constitution of the analogous compds. of α - $\text{HOCH}_2\text{CH}_2\text{CO}_2\text{H}$, it has been shown that there is only 1 basic Hg crotonate and that it contains the Hg atom in the benzene ring para to the phenolic OH. A soln. of 20 g. yellow Hg^{2+} in 20 cc. AcOH was added to 100 cc. and boiled free from excess AcOH was added to a soln. contg. 40 g. Na crotonate. The ppt. was filtered off and washed, yielding a true Hg salt, $[\text{MeC}_2\text{H}_4(\text{OH})\text{CO}_2]\text{Hg}$ (I). In boiling soln., I is decomposed to the basic Hg crotonate (II), $\text{MeC}_2\text{H}_4(\text{OH})\text{CO}_2\text{Hg}$.

Treatment of 20 g. II with 7.4 g. KCN in 100 cc. H_2O gave a series of fractions of crystals in 9.9, 3.5, 7.7 and 4.1 g. yields which, by analysis, only in

H₂O and behavior on nitration, proved to be identical samples of *K cyanoacrylate*, $\text{MeC}_2\text{H}_4(\text{OH})(\text{HgCN})\text{CO}_2\text{K}$ (III). Nitration of III or II by boiling with HNO_3 produced 3,2,6-Me(HO)(NO₂)C₂H₄CO₂H (IV). The constitution of IV was proved by reduction to the corresponding aminocarmic acid (V), m. 300°, by the aid of $\text{Na}_2\text{S}_2\text{O}_4$. Diazotization of V yielded 3,2,6-Me(HO)C₂H₄CO₂H, m. 215°, which was decarboxylated, by heating, to 1,4-dihydroxytoluene, m. 125°. Decarboxylation of V at 300° under reduced pressure yielded 1-hydroxy-4-aminotoluene, m. 175°. From the established constitution of IV and the assumption that, in nitration, the group NO_2 takes the place of the radical HgCN , a structure for III is postulated from which II is arrived at by the splitting out of KCN . The decomn. of I in boiling concn. takes place by cleavage to II and *o*-cregotic acid.

C. R. Addison



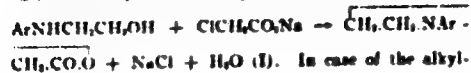
The use of the cyanohydrin method for the synthesis of alcamine acids (hydroxyalkylamine acids). A. P. Kuznetsov and N. A. Raashkov. *J. Gen. Chem.* (U. S. S. R.), 7, 1102-32 (1937).—Instead of the normal condensation of the nitrile when $\text{NHCH}_2\text{CH}_2\text{OH}$ (I) is condensed with HCl and KCN , the product is 1-phenyl-2-methyl-tetrahydrooxazole. Similarly, with AcCl I gives 1,2-dimethyltetrahydrooxazole, with MeCOCl , 1,1,2-trimethyltetrahydrooxazole, and with MeCOCl , 1,1,2-trimethyltetrahydrooxazole, 6, 72-61. HCl and hydroxypropylamine condense under the same conditions to 1

AS 4-11A DETAILING LITERATURE CLASSIFICATION

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The N-alkyl- and the N-arylmorpholones (2-ketotetrahydro-1,4-oxazines). A. I. Kipchanov, A. P. Tisel'ski and I. K. Usheiko. *Trudy Akad. Nauk. Gendarm. Univ.* 3, 45-52 (1938); *Khim. Referat. Zhur.* 2, No. 4, 54-5 (1939). - By heating the alkyl- and the arylaminomorpholones with $\text{ClCH}_2\text{CO}_2\text{Na}$ were obtained Me, Et, Pr, iso-Pr, iso-Am, PhCH₂, Ph and o- and p-Me-CH₂ derivs. of morpholone. In case of the aryl derivs. morpholones are formed directly



aminomorpholones the hydroxyalkylamino acids are formed first and are dehydrated to the corresponding alkylmorpholones by distn. *in vacuo*. The alkylmorpholones are easily hydrolyzed. By the action of concd. NH_3 on the arylmorpholones the amino acids, N-aryl-N'-dihydroxyethylaminoacetic acids, were obtained. The product of the condensation of N-phenylmorpholone with Meier's ketone was obtained in the form of an amorphous solid.

Its probable structure is $\text{Me}_2\text{NCCH}_2\text{CR}(\text{CH}_3)_2\text{NMe}_2 + \text{I}$ ($\text{R} = \text{p-CH}_3, \text{CH}_3, \text{O-CO-CH}_3, \text{NCH}_2\text{CH}_2\text{CH}_3$). For the prepn

of N-methylmorpholone 17 g. of $\text{ClCH}_2\text{CO}_2\text{H}$ in 35 cc. of water are neutralized with concd. NaOH , boiled for 7 hrs. with 13.5 g. of $\text{MeNHCH}_2\text{CH}_2\text{OH}$, evapor. on a water bath and the residue distd. *in vacuo*. The yield was 8.4 g., colorless liquid, b. 100-2°, b. 231° (Knoor, Ann. 307, 100 (1900)). A yield of 14 g. of N-ethylmorpholone (14 g. from 15 g. of $\text{EtNHCH}_2\text{CH}_2\text{OH}$) (Knoor and Schmidt, Ber. 31, 1076 (1898)), colorless mobile liquid, b. 97-98°. By hydrolysis was obtained N-ethyl-N'-dihydroxyethylaminoacetic acid, colorless crystals. A yield of 8 g. of N-propylmorpholone was obtained from 17 g. of propyl-ethanolamine, b. 131-0°, as a dense colorless liquid. N-Propyl-N'-dihydroxyethylaminoacetic acid is a non-crystg. sirup. The Cu salt $\text{C}_6\text{H}_{13}\text{N}_2\text{Cu}(\text{OH})_2$ forms dark blue needles. A yield of 2.5 g. of N-isopropylmorpholone was

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obtained from 7 g. of isopropylaminocetane, b. 54°. A yield of 8 g. of *N*-isopropylmorpholine was obtained from 11 g. of isopropylaminocetane, b. 150°. A yield of 11 g. of *N*-benzylmorpholine was obtained from 12 g. of benzylaminocetane (boiling for 15 hrs.), b. 155°. *N*-Phenyl-*N*- β -hydroxyethylaminocetic acid was obtained from *N*-phenylmorpholine (III) [Kiprianov, C. A. 24, 1064] with concd. NH_3 . The methyl ether of *N*-phenyl-*N*- β -hydroxyethylaminocetic acid yields III during the distn. *in vacuo*. From the reaction of 105 g. of *o*-toluidine and 14.7 g. of ethylene oxide in a sealed tube at 100° for 8 hrs. was obtained *N*- β -hydroxyethyl-*o*-toluidine (IV) in the form of a yellow oil, b. 168-71°. By boiling 32 g. of IV for 8 hrs. *N*- β -tolylmorpholine, b. 170-7°, was obtained. *N*- β -Hydroxyethyl-*N*-*o*-tolylaminocetic acid was obtained in the form of colorless needles, m. 113-14°. From *p*-toluidine and ethylene oxide was obtained *N*- β -hydroxyethyl-*p*-toluidine (V), b. 181-92° and m. 30°. From V white crystals of *N*- β -tolylmorpholine were obtained, m. 74-8° (sealed tube). White crystals of *N*- β -tolyl-*N*- β -hydroxyethylaminocetic acid were obtained from alk., m. 170-2°.

W. R. Henn

CA

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The substitution of hydrogen by the methyl group in the polymethylene chromophore of cyanine dyes. A. I. Kiptanov and N. G. Grigor'eva. *Trudy Khim. Sovetsk. Inst.* 3, 51-60 (1959); *Khim. Refrat. Zhur.* 2, No. 4, 86 N (1959). In order to observe the influence of the Me group as a substituent in different positions of the chromophores of the thiacyanines, investigations were made of thiacyanines proper, thiacarboyanines and thiodicarboyanines. (In the following formulas

$$R = \begin{array}{c} S - C \\ | \\ C_6H_5.NMe \end{array}, R' = \begin{array}{c} -C-S \\ | \\ NEt.C_6H_5 \end{array} \text{ and } R'' = \begin{array}{c} S - C \\ | \\ C_6H_5.NEt \end{array}$$

7-Methylthiacyanine, RCM₂R' (I), was obtained by the condensation of the methiodide of 1-methylmercaptobenzothiazole (II) with the methiodide of 1-ethylbenzothiazole (III) (Brit. pat. 436,550, C. A. 39, 4509). 7-Methylthiacarboyanine, R'CM₂R' (IV), was obtained from R'CH₂CHNPhAc (V) (Brit. pat. 344,402) and III, 8-methylthiacarboyanine by the method of Hamer (C. A. 23, 1903; 34, 1370), the 7-methylthiodicarboyanine (R'CM₂CHCH₂CHCH₂R') (VI) from R'CH₂CHCH₂CHNPh (VII) (Fr. pat. 774,028, C. A. 29, 2106) and III, 8-methylthiodicarboyanine (VIII), from the acetal of the tetraaldehyde and 1-methylbenzothiazole-5-yl (IX), and 9-methylthiodicarboyanine ac-

ording to Brit. pat. 381,904 (C. A. 27, 4769). The absorption curves were detd. for all dyes in a König-Martens spectrophotometer. The max. of absorption of I coincides with the curve of the unsubstituted thiacyanine. The max. of IV approaches the max. of the unsubstituted thiacarboyanine while the absorption curve of 8-Me deriv. is moved into the short-wave region. All curves of the thiodicarboyanines are very close to each other. The Me group has weakly bathochromic properties. For the prepn. of 2-methyl-2'-ethylthiacyanine iodide, C₁₂H₁₂N₂SI, 1 g. of II, 1 g. of 1-methylbenzothiazole-5-yl and 1 g. of AcONa (anhyd.) in 20 cc. of ethanol were boiled for 1 hr. From alc. were obtained yellow needles, m. 270.5°. For the prepn. of 2,7-dimethyl-2'-ethylthiacyanine iodide, C₁₄H₁₄N₂SI, 1 g. of III, 1 g. of II and 1 g. of AcONa were heated for 1 hr. in 25 cc. of absolute ethanol. From alc. the m. p. was 278.5° (decomp.).

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ASAC-55A METALLURGICAL LITERATURE CLASSIFICATION

with a yield of 24%. For the prepn. of 2,2'-diethyl-7-methylthiadicarbocyanine iodide, $C_{21}H_{25}N_3S_2I$ (IV), 0.6 g. of V and 0.5 g. of III were heated for 1 hr. in 3 cc. of pyridine. Fine blue-green crystals were obtained in 16.2% yield. For the prepn. of 2,2'-diethyl-7-methylthiadicarbocyanine iodide (VI) 0.1 g. of VII and 0.1 g. of III were boiled for 5 min. in 5 cc. of abs. alc. with 15 drops of piperidine. Fine green crystals with a yield of 11.5% were obtained. For the prepn. of 2,2'-diethyl-8-methylthiadicarbocyanine iodide (VIII) 0.5 g. of IX and 0.2 g. of tetrolaldehyde were heated for 30 min. to boiling in 10 cc. of pyridine. The pyridine was evaporated off and green crystals with a yield of 5% were obtained. W. R. Henn

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13

Estimating dihydroxybenzenes from aqueous solutions.
O. B. Zolotarev, A. I. Karginov, O. V. Narov and
M. M. Gerasimov, *Izv. VNIIT*, September 30, 1959.
Dihydroxybenzenes if used as the solvent at 80° and higher in a
bottle or container app. with the addn. of inorg. salts to
the soln. to be anal. to lower the soly. of dihydroxybenzenes
in water.

ASAC-SLA METALLURGICAL LITERATURE CLASSIFICATION

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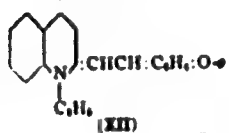
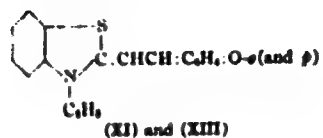
The relation between the structure and the color of unsymmetrical cyanine dyes. A. J. Kapanian and G. I. Polyakov. *Russk. Vsesoyuz. Akad. khimichesk. iuz. 1930, Moscow 1930, No. 3, 4, (a) 1; Akad. Referat Zhur. 1930, No. 7, 105 1.* The unevenness of rings of the polymethine chain, which possess the heterocyclic groups, makes possible a quantum transition in the middle of the dye. From the consideration of quantum transition as a whole for color in the visible spectrum, it can be expected that for asymmetrical dyes a weakening of the color occurs, i. e., a displacement of the max. of absorption to the short-wave region. In 11 of 13 unsymmetrical dyes (27 trimethine was and 3 pentamethine) the main max. of absorption was between the 2 max. of the 2 corresponding symmetrical dyes. In 10 cases a displacement toward the short wave region was observed. The second phenomenon was especially noticeable when the heterocyclic rings differed greatly in their aromatic characteristics or in the basicity of the heterocyclic N. Thus, the weakening of the color in the middle was found to be connected with its asymmetry. This verifies the conception of quantum transition as a cause of color in the cyanine dyes. W. R. H. H.

Hydroxystyryl derivatives of quaternary heterocyclic salts. A. I. Kiptirsky and V. K. Petrun'kin. *J. Gen. Chem.* (U. S. S. R.) 10, (1940) 12(1940).--Condensation of 1- and 4-hydroxybenzaldehyde with quaternary salts of 2- and 5-methylthiazole with quaternary salts of 2-methyl-4-dimethylthiazole, 2-methyl-4-phenylthiazole, 2-methyl-4-phenylthiazole, in the presence of pyridine yields the following yellow or orange compds.: 1-ethyl-2-(4-hydroxystyryl)-2-methylthiazolium iodide (I), m. 257-8°, absorption max. 394 mμ; 2-hydroxystyryl isomer (II), m. 215°, absorption max. 394 mμ; 1-ethyl-2-(4-hydroxystyryl)-5-phenylthiazolium iodide (III), m. 222-3° (decompn.), absorption max. 400 mμ; 1-ethyl-2-(4-hydroxystyryl)-5-benzothiazolium iodide (IV), m. 210°, absorption max. 420 mμ, and 2-hydroxystyryl isomer (V), m. 211° (decompn.), absorption max. 410 mμ. With quinoline, the reaction has to be carried out in abs. alc. in the presence of piperidine when there are formed 1-ethyl-2-(4-hydroxystyryl)quinolinium salts (VI), m. 232-3°, and the 2-hydroxystyryl isomer (VII), m. 194-205°. The above salts of the hydroxystyryl compds. yield on treatment with alkali the corresponding bright orange or deep red bases such as VIII 2H₂O from I, m. 178° (decompn.), IX 2H₂O from II, m. 173° (decompn.), X from III, m. 141-5° (decompn.), XI from V, m. 140-55° (decompn.), and XII from VII, m. 160-3° (decompn.). The base obtained from VI which is not intensively colored is rather unstable and has not been investigated further. When

IV was treated with alkali lye, the expected base was not obtained, since the base was very sensitive toward alkali and was decompd. immediately. When IV was treated with NaHCO₃, however, a mod. compd. of IV and the corresponding base XIII was obtained, m. 219-20° (decompn.). 2-(4-Dimethylaminostyryl)-1-ethyl-5-methylthiazolium iodide, m. 241° (decompn.), absorption max. 470 mμ, was prepd. from 2,4-dimethyl-1-ethylthiazolium iodide and 4-dimethylaminobenzaldehyde on heating in the presence of pyridine and piperidine. Detailed data are given on the absorption of the salts of the hydroxystyryl compds. and the corresponding bases in various solvents such as alc., CHCl₃, pyridine and water.

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Gertrude Herend

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The effect of solvent upon the color of organic dyes
A. I. Kuznetsov, and V. K. Petrun'kin *J. Gen. Chem.*
(U. S. S. R.) 10, 613 (1934). From a comparison of the
structures of the colored bases of hydroxyethyl dyes of
quaternary heterocyclic salts with those of other dyes
(tetramethyldiaminobenzene, some dyes of indigo, etc.)
it is concluded that the color changes in these dyes in
which there is possible a resonance between nonpolar struc-
ture and bipolar-ion structure. The mesomeric structure
of the dye and approaches one or other form, depending
on the dielectric constant of the solvent. A. A. Polgany

Inst. Chem., Khar'kov State U.

CA

The absorption spectra of cyanine dyes in the ultra-violet region. A. A. Kuznetsov and V. R. Potvin'kin. *J. Gen. Chem.* (U. S. R. R.) 10, 630 (1940). The absorption spectra of 7 sym. carbanilines and of 7 quaternary salts of heterocyclic bases from which the carbanilines were prepared. (salts of quinoline, 2-methylquinoline, 2-methylbenzoxazole, 2,3-dimethylbenzoxazole, 2,3,4-trimethylbenzoxazole, 2,4-dimethylthiazole and 2-methylthiazole) were investigated in the ultraviolet region. The absorption curves of dyes and corresponding salts were nearly similar in form and location. The ultraviolet absorption lines, together with the lines of the visible region, shifted toward the red with increase of the length of the polymethine chromophore of the cyanine dyes from benzothiazole to seven methine groups. The ultraviolet absorption of these dyes is conditioned by shifting of electrons in the heterocyclic rings.

3

A. A. Potvin'kin

Inst. Chem., Khar'kov State U.

CA

3

The color and symmetry in the structure of molecules of organic dyes. A. I. Kiprianov. *Doklady Akad. Nauk U. R. S. R.* 1940, No. 12, 3 17; *Khim. Referat. Zhur.* 4, No. 9, 49(1941); cf. *C. A.* 34, 4039. According to the quantum resonance theory, any change in symmetry in the mol. of salt-like methine dyes must be connected with the displacement toward the short waves of the absorption band. This is confirmed on cyanine dyes with 3 and 5 methine groups if the dyes contain certain heterocyclic components (indolenine, thiazole), or if the symmetry of the polymethylene chain is considerably distorted. Substituents introduced into one of the benzene rings of cyanine dyes do not result in hypsochromic displacements of the absorption band. Aryl groups substituted on heterocyclic N atoms have no appreciable effect, because they do not distort the electronic symmetry in the mol. W. R. Henn

RESEARCH LITERATURE CLASSIFICATION

10

Synthesis in the benzothiazole derivative series. A. I. Kirilany and G. V. Kirapal. *Uchenye Zapiski Khim. Sov. Unio.* 1940, No. 19, 305-11; *Khim. Refert. Zhur.* 4, No. 9, 63 (1941).—A no. of deriva., including, 2 monomethinecyanines, were obtained in expts. whose purpose was to study the acetylated deriva. of 2-mercapto-6-amino-benzothiazole as photographic stabilizers. 2-Mercapto-benzothiazole was used as the initial substance. A detailed scheme of the successive transformations and details of the synthesis are given. The following substances were obtained and described: 2-mercapto-6-amino-benzothiazole, m. 254-5°; 2-mercapto-6-acetamidobenzothiazole, m. 294-5°; 2-methylmercapto-6-acetamidobenzothiazole, m. 148-7°; 2-mercapto-6-benzamidobenzothiazole, yellow crystals, m. 231-4°; 2-methylmercapto-6-benzamidobenzothiazole, m. 194-7°; (2-mercapto-6-benzothiazolyl)urea, m. 340° (decomp.); 1,3-bis(2-mercapto-6-benzothiazolyl)urea, m. 304-6°; 2-methylmercapto-6-amino-benzothiazole, m. 110-11°; (2-methylmercapto-6-benzothiazolyl)urea, m. 168-6°; 1,3-bis(2-methylmercapto-6-benzothiazolyl)urea, m. 238-40°; (2-methylmercapto-6-benzothiazolyl)thiourea, m. 192-4° (decomp.); (3-ethyl-6-acetamido-2-benzothiazole); (3-ethyl-2-benzothiazole)methinecyanine iodide, m. 305° (decomp.), max. of absorption 437 mμ; (3-ethyl-6-benzamido-2-benzothiazole) (3-ethyl-2-benzothiazole)methinecyanine iodide, m. 293° (decomp.), max. of absorption 434 mμ, crystallizes with 2 H₂O. A similar phenomenon is observed for thioarocyanines with substituting H₂NH groups.

W. H. Henn

ASS-51A METALLURGICAL LITERATURE CLASSIFICATION

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| CA | | 17 | |
| <p>Making oil for noreels. Ya. A. Palkov, A. I. Kuznetsov and L. M. Sol'ts. <i>Khimiya i No. 1, 14-17 (1963)</i>.—Purified-free H_2O is freed from AcH, H_2O and $NaOH$ by washing with water, storing over 80% aq. $NaOH$ about 5 days and dist. Dry alkali is equally effective, but its heat of hydration (with H_2O in the H_2O) and its crystallizing effect are undesirable. App. is described and illustrated. On a lab. scale (6 kg.) the loss in this treatment (after recovering & out 10% unchanged) is 12-14%. Julian F. Smith</p> | | | |
| <p>ASD-3LA METALLURGICAL LITERATURE CLASSIFICATION</p> | | | |
| <p>1000 2000 3000 4000 5000 6000 7000 8000 9000 10000 11000 12000 13000 14000 15000 16000 17000 18000 19000 20000 21000 22000 23000 24000 25000 26000 27000 28000 29000 30000 31000 32000 33000 34000 35000 36000 37000 38000 39000 40000 41000 42000 43000 44000 45000 46000 47000 48000 49000 50000 51000 52000 53000 54000 55000 56000 57000 58000 59000 60000 61000 62000 63000 64000 65000 66000 67000 68000 69000 70000 71000 72000 73000 74000 75000 76000 77000 78000 79000 80000 81000 82000 83000 84000 85000 86000 87000 88000 89000 90000 91000 92000 93000 94000 95000 96000 97000 98000 99000 100000</p> | | | |

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5 g.) and 3.5 g. *p*-toluidic acid heated in pyridine for
 1 hr. gave *N*-(*p*-methoxyphenyl)benzothiazole-2,2'-di-
 24A" (from EtOH), lemon-yellow needles. This salt does
 not condense with $\text{H}_2\text{N}(\text{C}_6\text{H}_4)_2\text{NH}_2$ nor with $\text{H}_2\text{N}(\text{C}_6\text{H}_4)_2\text{NH}_2$.
 The products formed from homoterephthalic and homo-
 isophthalic acids may be considered to be analogs of cy-
 anine dyes in which the polymethylene chromophore was
 partially substituted by the benzene ring. The intensity
 and the depth of color in these compounds is considerably
 less than in the corresponding thiocyanines, probably due
 to the disturbance of the equivalence of the polar struc-
 tures existing in resonant condition. (I. M. Kuznetsov)

Index. Chem., AS, USSR

Color and structure of cyanine dyes. 1. Thiocarbonyl dyes with electropositive substituents. A. I. Kiprianov, I. K. Ushenko, and E. D. Sych (Acad. Sci. U.S.S.R., Moscow). *J. Gen. Chem. (U.S.S.R.)* 18, 300-6 (1948) (English summary); cf. *C.A.* 38, 1467. Electropositive substituents introduced symmetrically into the 6,6'-positions of thiocarbocyanine form by their bathochromic activity a series which corresponds to the mobility of their electron pairs. Acylation of the phenol or the amino group displaces the absorption max. to a shorter-wave region. Action of alc. alkali on benzoyl-amino and *p*-toluenesulfamido derivs. of thiocarbocyanine deepens the color; the second example gives 6 times greater effect than the first. The bathochromic action of pos. substituents can be explained by the formation of resonant structures with a neg. charge on the C atoms of the polymethine chain. *p*-Acetanilidine (190 g.) was treated with 111 g. P_2S_5 in 800 cc. $PhMe$ to yield 42% thiocarbocyanine, m. 116-18°; 67 g. of this, in 1200 cc. $N NaOH$, was added dropwise with stirring to a cooled soln. of 321 g. $K_2Fe(CN)_6$ in 800 cc. water at 8-10°; after stirring for 1 hr. the mixt. was filtered and the ppt. washed with water; after soln. in benzene, the product was dried by azeotropic distn. of the solvent, and distd. *in vacuo* to yield 28% 2-methyl-6-methoxybenzothiazole, b.p. 154-55°. Heating 10 g. of the base with 11 g. $Et p$ -toluenesulfonate for 6 hrs. at 180-40° gave 19.7 g. of the quaternary compd. as a red-brown, water-sol. solid mass. Heating with concd. HCl (18 hrs. at 180-80°) or concd. HI (6 hrs. at 120-80°) gave 2-methyl-6-hydroxybenzothiazole hydrochloride, m. 223-5° (decomps.) (isolated as dihydrate), $lit.$ m. 374-5°. 2-Methyl-6-alko-

benzothiazole (27 g.) in 150 cc. concd. HCl was heated on a steam bath, reduced with 34 g. Sn , and treated with an excess of 15% $NaOH$; extra. of the dried ppt. with hot $PhMe$ gave 79% of 2-methyl-6-aminobenzothiazole, m. 123° (lit. 155-6° from $EtOH$). Diazotization of 32.4 g. of this, treatment of the diazo soln. at 0° with 37.5 g. K cyanide with stirring, heating to 60-5° for 1 hr., taking up the bip. oil in $PhMe$, evapn. of the solvent *in vacuo*, boiling the residue with 35 g. KOH in 150 cc. $EtOH$ for 2.5 hrs., removal of $EtOH$, cooling, neutralization by HCl , and extra. with Et_2O gave 30% of 2-methyl-6-aminobenzothiazole, b.p. 109-9°, m. 48°. The success of prepn. depends on uninterrupted operations; the product oxidizes readily in the air. The following quaternary salts were prepd.: $Et p$ -toluenesulfonate (by heating with the ester for 2.5 hrs. at 120-30°) (no const. given); *no ethoxide* (by addn. of KI to aq. soln. of above salt) (no const. given); *methoxide* (by addn. of KI to aq. soln. of the dimethyl sulfate quaternary salt), m. 212° (from $EtOH$). 2-Methyl-6-iodobenzothiazole, m. 141-2°, was prepd. by diazotizing 2.5 g. of the amino deriv., treating with 4 g. KI , letting stand overnight, heating on a steam bath, making the mixt. alk., distg. the product under 5 mm., and recrystg. from C_6H_6 ; heating with $Et p$ -toluenesulfonate at 120-30° for 4 hrs., at 150° for 1 hr. gave the quaternary salt; the aq. soln. of this treated with KI gave the ethoxide, m. 227°. The following dyes were prepared: $Et(2$ -ethyl-6-methoxy-7-benzothiazole)resorcinolcyanine iodide, $C_{22}H_{21}N_3O_5S_2$, m. 376° (lit. 376°); 2-ethyl-2-methyl-6-methoxybenzothiazole *p*-toluenesulfonate and 3 g. orthoformic ester in 10 cc. pyridine were

heated to boiling for 25 min., evapd. to $1/2$ vol. and treated with dil. EtOH, convert to the iodide by means of KI, and recrystallize from EtOH. I (2.7 g.) was heated in a sealed tube with 5 g. concd. HBr at 120-30° for 5 hrs., dild. with water, excess HBr neutralized by NaOH, and the cryst. dye transformed into the iodide by heating with aq. KI; after 4 crystals from EtOH there was obtained 21% of *bis*(3-ethyl-4-hydroxy-2-benzothiazole)trimethinecaranine iodide, $\text{C}_{24}\text{H}_{22}\text{N}_4\text{O}_4\text{I}_2 \cdot \text{H}_2\text{O}$ (II), m. 234° (decoloration). *Bis*(3-ethyl-6-acetoxy-2-benzothiazole)trimethinecaranine, m. 256°, was prepd. by heating II with AcCl; action of alkali in EtOH even in the cold leads to hydrolysis of the Ac groups and the soln. changes from violet to blue. *Bis*(3-ethyl-6-mercapto-2-benzothiazole)trimethinecaranine *p-toluenesulfonate*, by heating 1 g. 3-ethyl-2-methyl-6-*p-toluenesulfonate*, by heating 1 g. 3-ethyl-2-methyl-6-mercaptobenzothiazole *p-toluenesulfonate* and 1 g. orthoformic ester in 10 cc. pyridine for 25 min., cooling, washing the ppt. with Et₂O, water, and EtOH gave 76% of a prod. m. 180° (from EtOH), but added 2 soln. of 10.6 g. CuSO₄ and 12.3 g. KCN in 100 cc. water, heated on a steam bath for 1 hr., neutralized, and dried to give 2, which was apparently an oxidation product and did not correspond to the analysis. *Bis*(3-ethyl-6-mercaptobenzothiazole)trimethinecaranine, m. 135° (from PhMe), was prepd. by treating 20 g. 2-methylbenzothiazole with 60 g. chlorosulfonic acid with cooling and stirring, heating for 4 hrs., to 140-45°, pouring onto ice water and benzene, sepp. the benzoic soln., and freeing of solvent; yield 84%; treatment with NH₃ gave the corresponding amide, m. 184-8°; boiling with water gave the corresponding sulfonic acid, m. 206°. The sulfonic acid was converted into the quaternary salt by heating with Et₃N in EtOH for 12 hrs. at 145-50°. The following thioarocarbazones were prepd. by heating the sulfonyl chloride with corresponding alc.: *Me*, m. 43° (from PhMe), *Et*, m. 88° (from EtOH), *Ph*, m. 124-5° (from EtOH); treatment of the chloride with Et₃NH gave the corresponding diethylamide, water-sol. brown mass which was not purified further; treatment of the chloride with PhNH₂ gave the amide, m. 120° (from EtOH); 1-naphthylamine gave the amide, m. 184-8° (from EtOH). 2-Methyl-6-mercaptobenzothiazole was diazotized, and the soln. of the *p-toluenesulfonate* was decolorized, and the acid was decolorized by heating with EtOH and the ppt. washed with water, and dried to give 2, which was apparently an oxidation product and did not correspond to the analysis. *Bis*(3-ethyl-6-mercaptobenzothiazole)trimethinecaranine, m. 135° (from PhMe), was prepd. by treating 20 g. 2-methylbenzothiazole with 60 g. chlorosulfonic acid with cooling and stirring, heating for 4 hrs., to 140-45°, pouring onto ice water and benzene, sepp. the benzoic soln., and freeing of solvent; yield 84%; treatment with NH₃ gave the corresponding amide, m. 184-8°; boiling with water gave the corresponding sulfonic acid, m. 206°. 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compn.). *Bis(3-ethyl-6-ethylsulfo-2-benzothiazole)trimethincyanine p-toluenesulfonate*, prepd. analogously, bronze plates, m. 227° (decomp.). *Bis(3-ethyl-6-amino-2-benzothiazole)trimethincyanine chloride*, from the quaternary salt and orthoformic ester in pyridine, treated with hot aq. KCl soln.; bronze crystals, m. 217° (decomp.) from EtOH. *Bis(3-ethyl-6-dimethylamino-2-benzothiazole)trimethincyanine perchlorate*, prepd. from pyridine soln. by NaClO₄, bronze powder, m. 186° (decomp.) from EtOH. *Bis(3-ethyl-6-phenylamino-2-benzothiazole)trimethincyanine chloride*, prepd. from pyridine soln. by NaCl, forms green needles, m. 146° (decomp.) from EtOH; *p-toluenesulfonate*, dark green powder (from 60% EtOH). *Bis(3-ethyl-6-naphthylamino-2-benzothiazole)trimethincyanine p-toluenesulfonate*, dark-brown powder from EtOH. *Bis(3-ethyl-6-cyano-2-benzothiazole)trimethincyanine iodide*, by treatment of the pyridine soln. with KI, coppery crystals, m. 273° (decomp.) from EtOH. *Bis(3-ethyl-6-amino-*

formyl-2-benzothiazole)trimethincyanine iodide, by treatment of pyridine soln. with KI; dark metallic crystals (from EtOH). *Bis(3-ethyl-6-carboxybenzothiazole)trimethincyanine iodide*, by soln. with KI; green metallic needles, m. 228° (decomp.) from EtOH. *Bis(3-ethyl-6-carboxy-2-benzothiazole)trimethincyanine iodide*, coppery crystals, m. 228° (decomp.) from MeOH. *Bis(3-ethyl-6-vinyl-2-benzothiazole)trimethincyanine iodide*, fine dark cherry colored needles, m. 243° (decomp.). Abs. max. (in m₀) for the 6,6'-substituents were: H 548, NH₂ 560, NHEt 561, SO₂ 561, SO₂OMe 561, SO₂OEt 562, SO₂NH₂ 563, SO₂NEt 564, SO₂OPh 567, SO₂NHPh 570, SO₂NPh 570, SO₂NH(C₆H₅) 570, CN 571, COMe 571, C₆H₅ 572, COO⁻ 572, CO₂Me 572, NO₂ 585. G. M. K.

M. I. M. I. Organic Chem., AS USSR, -1944.

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Colour and Constitution of Cyanine Dyes II. Thiocarbocyanines with Electronegative Substituents. A. I. KIRMANOV and I. K. USHAKOV. *J. Gen. Chem. U.S.S.R.*, 15, 207-14, 1945. (English summary). Describes thirteen new thiocarbocyanine dyes symmetrically substituted in the 6:6' positions by electronegative groups. A table lists the absorption maxima for these dyes and also for those derived by salt formation at the substituent group, e.g., NH_2^+ , COO^- , SO_3^- , etc. In each example a bathochromic shift is produced, this

being least for NH_2^+ and greatest for COO^- , COOC_2H_5 and NO_2 . This effect is considered to be due to the development of resonance structures with a negative charge on the substituent and a positive charge on the trimethine chain; this view is supported by the fact that these dyes are more rapidly decolorized by alkalis than the unsubstituted dye, whilst those with electro-positive substituents are decolorized more slowly.

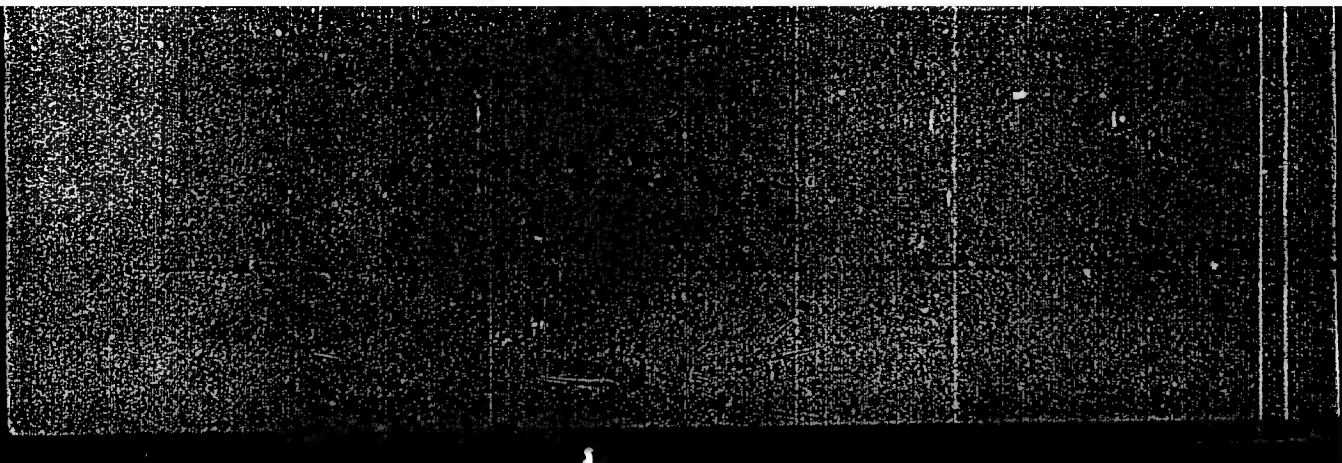
D.J.F.

Color and structure of cyanine dyes. III. Substituted thioarboyanines of unsymmetrical structure. A. I. Kuznetsov and I. K. Usbenko. *J. Gen. Chem.* (U.S.S.R.) 15, 644-9 (1945) (English summary); cf. *C.A.* 40, 2401. — Destruction of symmetry of cyanine dyes leads to displacement of the absorption band as it was first shown by K. and Pilyugin (*Uch. Zap. Kharkov Gosudarst. Univ.* 10, 91 (1937)). In the present paper the results of symmetry displacement by introduction of unequal substituents into 6,6-positions are given. In the presence of but one substituent, the absorption shift does not occur, while substitution of two unlike substituents produces a shift which is the greater, the more different are the substituents. The unsym. thioarboyanines were prepd. conventionally by heating one of the quaternary salts in AcOH with diphenylformamide, and the resulting intermediate was then condensed with the other quaternary compd. in boiling pyridine; the dyes were purified by cry-st. from EtOH. For the following compds., the found and calcd. values of the absorption max. are given: (3-Ethyl-6-methoxy-2-benzothiazole)trimethinecyanine iodide, green, m. 245° (decompn.), 596 mμ, 567 mμ; (3-ethyl-6-methoxy-2-benzothiazole)trimethinecyanine iodide, black, m. 215° (decompn.), 565 mμ, 565.5 mμ; (3-ethyl-6-nitro-2-benzothiazole)trimethinecyanine iodide, m. 263° (decompn.), 572 mμ, 571.5 mμ; (3-ethyl-6-dimethylamino-2-benzothiazole)trimethinecyanine iodide, violet, m. 254° (decompn.), 585 mμ, 585 mμ; (3-ethyl-6-nitro-2-benzothiazole)trimethinecyanine iodide, dark powder, m. 270° (decompn.), 578 mμ, 580.5 mμ; (3-ethyl-6-nitro-2-benzothiazole)trimethinecyanine iodide, dark-violet, m. 279° (decompn.), 574 mμ, 573.5 mμ; (3-ethyl-6-nitro-2-benzothiazole)trimethinecyanine iodide, green, m. 262 mμ, 561.5 mμ; (3-ethyl-6-nitro-2-benzothiazole)trimethinecyanine iodide (by hydrolysis of above by heating with H₂SO₄-AcOH on a steam bath for 2 hrs.), dark crystals, m. 258° (decompn.), 583 mμ, 591 mμ; (3-ethyl-6-nitro-2-benzothiazole)trimethinecyanine iodide, brown luster, m. 265° (decompn.), 588 mμ, 589.5 mμ. G. M. Koudatoff

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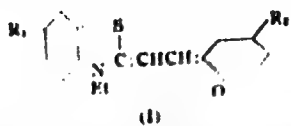
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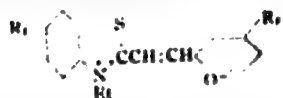
APPROVED FOR RELEASE: 09/17/2001

CIA-RDP86-00513R000722610006-7"

Effect of the solvent on the color of organic dyes. H. A. Klapachuk and E. S. Timonchenko (Kiev State Univ., Ukraine). *Zhur. Obshch. Khim.* (J. Gen. Chem.) 17, 1468-76 (1947) (in Russian); cf. C.A. 34, 773F. (1) Observed shifts of the max. of absorption, depending on the polarity of the solvent (H₂O and EtOH or CHCl₃ and CCl₄), of substituted intramolecular dyes of the type



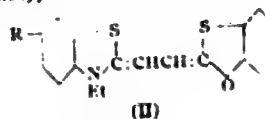
where R₁ and R₂ are OR and NMe₂ (electron donor groups) or NO₂ (electron acceptor). confirm the assumption that such shifts are due to the displacement of resonance between the above nonpolar form and the bipolar form



With R₁ = H, and R₂ = H, EtO, Me₂N, NO₂, the max. λ_{max} in H₂O, resp., at 495, 494, 501, 539 mμ, in EtOH at 552, 547, 542, --, in CHCl₃ at 590, 587, 580, --; with R₁ = H and R₂ = H, EtO, NO₂, in H₂O at 495, 512, 474, in EtOH at 532, --.

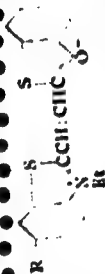
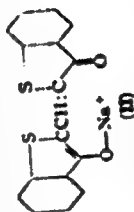
530-534 METALLURGICAL LITERATURE CLASSIFICATION

611, 513, in CHCl₃ at 590, 621, 620 mμ. An electropos. R₁ shifts the max. to shorter waves, an electroneg. R₁ to longer waves. On the other hand, an electropos. R₂ obviously favors the bipolar-ion form, an electroneg. R₂ the nonpolar form. In contrast thereto, a pos. R₂ should favor the nonpolar form, a neg. R₂ the ionic form, accordingly, a pos. R₂ shifts the max. to longer waves, a neg. R₂ to shorter waves. Substitution of a pos. R₁ and a neg. R₂ results in an accumulated strong hypsochromic effect, e.g., R₁ = EtO, R₂ = NO₂, max. in EtOH and in CHCl₃, 590 and 590, resp.; R₁ = Me₂N, R₂ = NO₂, 520 and 575. Substitution of NO₂ in both R₁ and R₂ has but little effect on the color (max. at 544 and 567 in EtOH and CHCl₃, resp.); EtO in both R₁ and R₂ gives, in H₂O, EtOH, and CHCl₃, max. at 525, 560, and 620 mμ, resp. The deriv. with R₁ = NO₂ and R₂ = EtO could not be isolated; under the action of NaOH on the corresponding hydrochloride, there appears a momentary deep color which, however, disappears rapidly. (2) In merocyanine dyes of the type



an electropos. R₁ enhancing the bimic structure

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PROCESSING AND PROPERTIES INDEX

1. 5. 2-methyl-9-ethoxybenzothiazole ethoxide, 0.35 g. methylhydrazide, and 3 ml. pyridine boiled 15 min. gave 1.02 g. of the iodide, from the aq. suspension of which NH_4OH pptd. dark brown $\text{C}_{11}\text{H}_{11}\text{O}_2\text{NS}$, m. 215-217°. $R_1 = \text{EtO}$, $R_2 = \text{NO}_2$; 0.5 g. 2-methyl-6-ethoxybenzothiazole ethoxide, 0.3 g. 2-hydroxy-5-nitrobenzoic acid, and 3 ml. pyridine boiled 20 min. gave directly 0.2 g. (after recrystallization from EtOH) dark red $\text{C}_{11}\text{H}_{11}\text{O}_2\text{NS}$, m. 228°. $R_1 = \text{EtO}$, $R_2 = \text{NO}_2$; 0.5 g. 2-methylbenzothiazole ethoxide, 0.3 g. 2-hydroxy-5-ethoxybenzothiazole ethoxide, and 3 ml. pyridine boiled 30 min. gave 0.02 g. of a red iodide, m. 228° from the aq. suspension of which NaOH pptd. $\text{C}_{11}\text{H}_{11}\text{O}_2\text{NS}$, m. 231°. $R_1 = \text{NO}_2$, $R_2 = \text{EtO}$; 0.5 g. 2-methyl-6-ethoxybenzothiazole ethoxide, 0.3 g. 2-hydroxy-5-ethoxybenzothiazole ethoxide, and a few drops of pyridine boiled 30 min. gave 0.6 g. (80%) orange $\text{C}_{11}\text{H}_{11}\text{O}_2\text{NS}$, m. 233°. 5 ml. abs. alc., and a few drops of NH_4OH the color disappears instantaneously, giving a dark brown ppt. on treatment of the aq. soln. with alkali or NH_4OH the color disappears instantaneously, giving a dark brown ppt. which dissolves in H_2O , EtOH , and EtO with the same yellow color. $R_1 = \text{EtO}$, $R_2 = \text{EtO}$; 0.5 g. 2-hydroxy-5-ethoxybenzothiazole ethoxide, and 2 ml. pyridine boiled 30 min. gave 0.3 g. of an orange iodide; of this, 0.1 g. in suspension in H_2O treated with NaOH , pptd. 0.1 g. dark $\text{C}_{11}\text{H}_{11}\text{O}_2\text{NS}$, m. 110°. (4) The following are the syntheses of the derivatives of II: $R = \text{H}$: 0.8 g. diethyl barbituric acid, 1 g. 3-hydroxythiophenecarboxylic acid, and 5 ml. abs. alc. boiled 1 hr. pptd. 0.5 g. brown $\text{C}_{11}\text{H}_{11}\text{O}_2\text{NS}$, m. 160°; 0.4 g. of this intermediate, 0.5 g. 2-methylbenzothiazole ethoxide, and 0.14 g. anhyd. AcONa , boiled in abs. alc. 1 hr., gave 0.45 g. $\text{C}_{11}\text{H}_{11}\text{O}_2\text{NS}$, m. 216-218°. $R = \text{NO}_2$: 0.5 g. 2-methyl-6-nitrobenzothiazole ethoxide, 0.36 g. of the above intermediate, 0.14 g. anhyd. AcONa , and 10 ml. abs. alc. boiled 1 hr., gave 0.11 g. (65%) of dark brown $\text{C}_{11}\text{H}_{11}\text{O}_2\text{NS}$, m. 241-243° mol. in H_2O and slightly sol. in EtOH . $R = \text{Me}$: 0.5 g. 2-methyl-6-nitrobenzothiazole ethoxide, treated as above, gave 0.44 g. of a dark violet powder; $\text{C}_{11}\text{H}_{11}\text{O}_2\text{NS}$, m. 202°. $R = \text{EtO}$: in this same way, 0.5 g. 2-methyl-6-ethoxybenzothiazole ethoxide, N° Thm crystalline, $\text{C}_{11}\text{H}_{11}\text{O}_2\text{NS}$, m. 227-228°.

ASB-51-A METALLURGICAL LITERATURE CLASSIFICATION

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KIPRIANOV, A. I.

Kiprianov, A. I., and Ushenko, I. K.- "Oxidation of the Quarternary Salts of Dibenztiasolyl and Dibenzoxasolylpropane into Carbocyanines" (p. 1542)

SO: Journal of General Chemistry, (Zhurnal Obshchei Khimii), 1947, Vol. 17, No. 8

N-Phenylthioacetamide. A. I. Kirilov and I. K. Usenko. *J. Gen. Chem. (U.S.S.R.)* 17, 2301-7 (1947) (in Russian).—A very much simplified procedure for N-phenylbenzothiazole consists of treatment of a benzene solution of o-PnNHCl₂ with an acyl chloride; the corresponding 2-alkyl-3-phenylbenzothiazolium chloride precipitates immediately and is readily converted to the corresponding iodide. In the case of the 2-Me deriv., obtainable by AcCl, the yield is 20%, 10 times that obtained by the older method (Lit. 551,230 (C.A. 38, 2281)). In addition, attempts to repeat the prep. of 2-methyl-3-phenylbenzothiazolium iodide under conditions

given in the patents (see above), using iodine in AcOH or MeCNPh, failed to give the desired product. 2-Phenylbenzothiazole (34 g.), 48 g. KOH, and 250 ml. EtOH, heated on a steam bath 3 h., then freed of EtOH, and the residue neutralized with HCl and acid. with EtOH, gave 77%; o-(phenylamino)thiophenol, b.p. 174-5° (usually 175-6°), m.p. 102°. This (67%) was also oxidized to the disulfide, m. 102°. 2-Phenyl-3-aminobenzothiazole made by heating 34 g. 3-phenyl-3-aminobenzothiazole with 60 g. KOH in 125 ml. EtOH on a steam bath 4.5 hrs. The product, with acyl chlorides (equimolar amounts) in benzene gave either the crystalline quaternary 3-phenyl-2-alkylbenzothiazolium chloride or a rapidly freezing oil; evapn. of the mist, and treatment of the residue in EtOH with KI gave the corresponding iodides as microcrystals. The following were prep. (the 2-alkyl in italics): 2-methyl iodide, from AcCl, m. 234°, 4% yield; 2-ethyl iodide, from EtCOCl, m. 225°, 40%; 2-propyl iodide, from EtCOCl, m. 214°, 31%; 2-isobutyl iodide, from EtCOCl, m. 162°, 24%. EtCOCl gave the 2-(isobutyl) iodide, mixed with only 4-phenyl 3-benzothiazole;

the mist. is readily split by the water in the former comp. (no phys. constants of the products are given); the yield of the former is 18%. Condensation of the above iodides with KI orthodromate, orthodromate, or orthodromate by boiling for 0.25 h. in pyridine, followed by pptn. with EtOH or water, gave the following thiocarbonyl iodides. Iodides: 2,3'-diphenyl, m. 276° (from EtOH), 70%, green, also max. 565 mμ; 2,3'-diphenyl-2-methyl, m. 242° (from EtOH), cherry red, max. 551 mμ, 60%; 2,3'-diphenyl-2-ethyl, m. 221° (from EtOH), cherry red, max. 541 mμ, 60%; 2,3'-diphenyl-2-isobutyl, m. 210° (from EtOH), max. 541 mμ, 72%; 2,3'-diphenyl-2-tert-butyl, m. p. not given, also max. 542 mμ, 60%; 2,3'-2,3'-tetraphenyl, m. 312° (from EtOH) (AcCl used for condensation as pyridine does not work), also max. 542 mμ, 25%. Reaction of 2,3'-diphenyl-2,3'-dichloro, m. 251° (from EtOH), 100%, green, also max. 547 mμ, 17%; 2,3'-diphenyl-2,3'-dichloro-2-methyl, m. 220° (from EtOH), green, max. 543 mμ, 21%. Condensation of the 2-alkyl-3-phenylbenzothiazolium iodides with p-MeNC₆H₄Cl in AcOH readily gave the following benzothiazolium iodides: 2-phenyl-2-(p-dimethylaminophenyl), m. 218° (from EtOH), blue-violet, also max. 547 mμ; 2-phenyl-2-(p-dimethylaminophenyl), m. 196° (from EtOH), red, max. 544 mμ, 51%; 2-phenyl-2-(p-dimethylamino-2-ethylphenyl), m. 175° (from EtOH), also max. 511 mμ, 50%; 2-phenyl-2-(p-dimethylamino-2-phenylphenyl), m. 165° (from EtOH), also max. 530 mμ, 35%; 2-phenyl-2-(p-dimethylamino-2-bromophenyl), m. p. not given, violet crystals, too oil. for recrystn., 72% yield, also max. 540 mμ. A strong bathochromic effect is evident in 3-phenyl-2-alkyl-3-phenylbenzothiazolium iodides and a very strong effect in 2,3-alkylated derivatives of the thiocarbonyl iodides listed above. (I. M. K.)

KIPRIANOV, A. I.

Kiprianov, A. I. and Rozn, Yu. S. "Synthesis of N-allyl-akriiones", Ukr. khim. zhurnal, 1948, Issue 1, p. 17-20, - Bibliog: 7 items.

SC: U-3042, 11 March '53, (letopis 'nykh Statey, No. 10, 1944).

KIRRIANCY, A. I.

Kirriancov, A. I. and Fridman, S. G. "Quaternary heterocyclic anorethine salt derivatives", Ukr. khim. zhurnal, 1948, Issue 1, p. 29-44, - Bibliog: 15 items.

SC: U-3812, 11 March 53, (Ietopis 'nykh Statey, No. 10, 1948).

KIPRIANOV, A. I.

Ussr/Chemistry - Cyanine Dyes
Chemistry - Cyanines

Feb 1946

"N-arythiazolopyrimidines," A. I. Kiprianov, F. I. Amine, I. K. Ushenko, Inst Org Chem, Acad Sci Ussr, 34 pp

"Zhur Obshch Khim" Vol XVIII (LXXI), No 2

Todd's, Bergel's, and Karimullah's methods were used in condensation of chloroacetone with thioacetone, produced aniline, alpha-naphthylamine, p-anisidine, and p-methoxyaniline. As a result authors obtained perchlorates of 3-phenyl-, 3-alpha-naphthyl-, and 3-p-dimethylaminophenyl-2,4-dimethylazole. By synthesis these produced symmetrical and asymmetrical cyanide dyes. Established strong effect of radical in heterocyclic nitrogen on absorption of asymmetrical carbocyanine, which contains thiozole and benzothiazole nucleus. Submitted 23 Sep 1946.

6849

KIPRIANOV, A. I.

Author: Kiprianov, A.I.

Title: Electronic Theory in Organic Chemistry. 2 Revision
diagram.

Date: 1949. Kiev

Subject: 1. Atomic Theory 2. Electronics 3. Chemistry

Available: Library of Congress, Call No: CD461.24. 1949

Source: Lib. of Cong. Subj. Cat., 1950

KIPRIANOV, A.I.; PAZENKO, Z.H.

Synthesis of benzo-1, 4-thiazine quaternary salts. Dep. AN URSS no.3:
9-14 '49. (MIRA 9:9)

1. Institut organichnoi khimii AN URSS. 2. Diysniy chlen AN URSS (for
Kiprianov). (Benzothiazine)

KIPRIANOV, A.I.; PAZENKO, Z.N.

Cyanine dyes and styryls of the benzo-1, 4-thiazine series. Dop. AN
URSR no.3:15-21 '49. (MLRA 9:9)

1. Institut organicheskoi khimii AN URSR. 2. Diysniy chlen AN URSR
(for Kipriyanov).
(Benzethiazine) (Cyanine dyes)

25

Cyanine dyes from isomeric 2-methyl-hydroxybenzothiazoles. A. I. Kuznetsov and N. I. Mashevskaya. *Zhur. Khim. Khim. (J. Chem. Chem.)* 19, 1126 (1949). 2-Methyl-7-methoxybenzothiazole (1 g.) and 1 g. 48% HBr after 6 hrs. in a sealed tube at 145-151° gave 33% 2-methyl-7-hydroxybenzothiazole, m. 192° (from EtOH). The 6-*HO* isomer, obtained similarly at 120-130°, was isolated as the HBr salt, m. 274-8°, as the HCl salt (precip. by using concd. HCl) 18 hrs. at 150-160°, m. 335-8°; the free base, obtained from the salts, was crystal. from MePh (no m.p. given); hydrolysis of 2-methyl-6-methoxybenzothiazole ethoxide by concd. HBr at 130-5° gave the HBr salt cited above. Heating the 6-*HO* isomer with EtI in 110-15° 12 hrs. gave the ethoxide, m. 290° (from EtOH), while AcO after 3 hrs. on a steam bath gave the Ac deriv. of the base, m. 90-100° (from EtOH), in 83% yield. Similar method gave 2-methyl-5-hydroxybenzothiazole, 82%, m. 187° (from MePh), whose Ac deriv., m. 93-4° (from EtOH), and the 4-*HO* isomer, m. 145° (from MePh), whose HBr salt, m. 265°, and the Ac deriv., m. 79° (from 50% EtOH), was obtained in 80% yield by Rebotton-Baumann procedure with AcO and 10% NaOH. 2-Methyl-7-hydroxybenzothiazolium Et p-toluenesulfonate (0.8 g.), 0.8 g. Et orthodumate, and 4 ml. pyridine boiled 1 hr., dil., and treated with KI gave 9% but 3-ethyl-7-hydroxy-2-benzothiazolylmethine isomer, m.p. decomp. 251-3° (from EtOH), also obtained in 34% yield by cleavage of the MeO groups in the di-MeO analog by 48% HBr at 140-50°; the product has absorption max. at 564 mμ in neutral soln. and 560 mμ in alk. soln.

Similarly, 2-methyl-6-hydroxybenzothiazole ethoxide gave 20% but 3-ethyl-6-hydroxy-2-benzothiazolylmethine isomer, m.p. decomp. 204° (from EtOH) (contains 11% on cryst.); its di-Ac deriv. was obtained by a similar condensation of the MeO deriv. in 40% yield, decomp. 290-91° (from EtOH); the product has absorption max. 576 mμ in neutral, 618 mμ in alk. soln., while di-Ac deriv. gives 562 mμ. The 5-*HO* analog obtained by hydrolysis of the diAc deriv. by alk. KOH at room temp. was not isolated in solid form, but its maxima were 575 mμ in neutral and 612 mμ in alk. soln.; the di-Ac deriv., prep. by condensation of 2-methyl-5-acetylbenzothiazole 1:1 p-toluenesulfonate as above in 24% yield, decomp. 213-15° (from EtOH), had an absorption max. at 567 mμ. The 4-*HO* analog prep. from the corresponding Et p-toluenesulfonate in 13% yield, formed violet crystals (no m.p. given), having absorption max. at 563 mμ in neutral and 562 mμ in alk. soln.; the di-Ac deriv. (by similar condensation of the Ac deriv.) obtained in 13% yield, decomp. 266-7°, absorption max. 562 mμ. Boiling for 1 hr. 1 g. 2-methyl-6-hydroxybenzothiazole Et p-toluenesulfonate

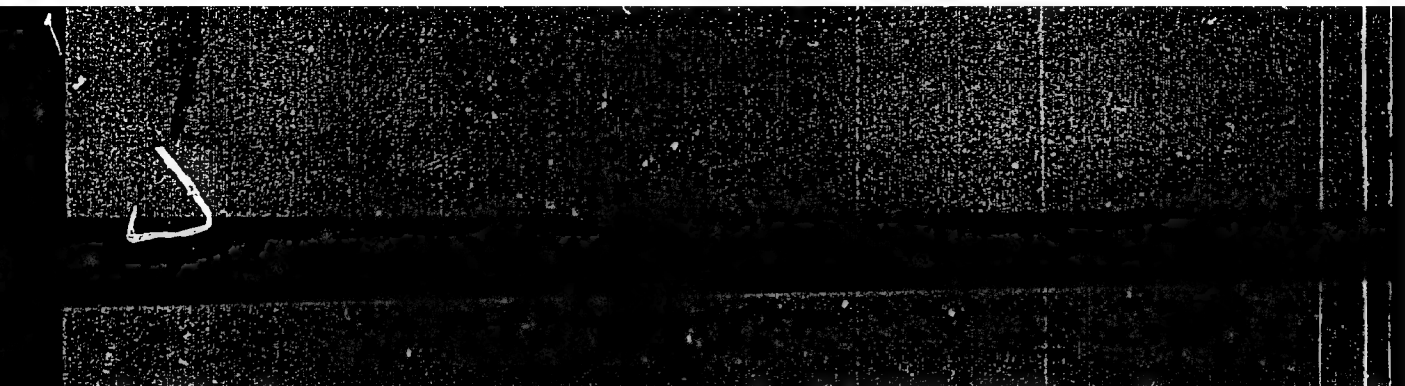
with 1.2 g. 3-(α -acetamidobenzyl)benzothiazole and 4 ml pyridine gave 21% (3-ethyl-2-benzothiazole)(3-ethyl-6-hydroxy-2-benzothiazole)methanesulfonate, decomp. 215° (from EtOH), having absorption max. at 568 m μ in neutral and 564 m μ in alk. soln.; the product contd. 11% of cryst. Similarly, the 2-methyl-5-acetylbenzothiazole Et ρ -toluenesulfonate gave 17% (3-ethyl-2-benzothiazole)(3-ethyl-5-hydroxy-2-benzothiazole)methanesulfonate, after treatment of the di-Ac deriv. by alc. KOH at room temp.; the di-Ac deriv. decomp. 275.6° (from EtOH), with an absorption max. at 564 m μ , the HO deriv. (not described), had 567 m μ in neutral and 577 in alk. solns. The 4-HO analog, obtained similarly in 20% yield, gave max. 560 m μ in neutral and 563 m μ in alk. solns., while the di-Ac deriv., obtained in 10% yield, decomp. 263-4°, gave 558 m μ max. Isolating 0.5 g. 2-acetylbenzothiazole Et ρ -toluenesulfonate, 0.6 g. 2-(α -acetamidobenzyl)-3-ethyl-6-nitrobenzothiazole ethanediol and 5 ml pyridine 45 min. gave 21% (3-ethyl-6-hydroxy-2-benzothiazole)(3-ethyl-6-nitro-2-benzothiazole)methanesulfonate, decomp. 278-9° (purified by washing with hot EtOH), which on addn. of alkali gives the hydroxy nitro deriv. with change of color, with a shift to the shorter wavelengths by 12 m μ . G. M. K.

Synthesis of quaternary salts of benzothiazole. A. I. Kiprianov and Z. N. Puzenko *Zhur. Obshch. Khim.* (J. Gen. Chem.) 19, 1515-22 (1949). Quaternary salts of benzothiazole derivs. are readily obtained by the reaction of acyl halides with *N*-substituted *o*-aminothiophenols. Addn. of 0.8 g. AcCl in 2 ml. C_6H_6 to 1.39 g. *o*- MeNH - $\text{C}_6\text{H}_4\text{SH}$ (I) in 5 ml. C_6H_6 and cooling gave hygroscopic 2-methylbenzothiazole-*MeI*, which with aq. KI gave the corresponding methiodide, m. 221-2° (from H_2O), in 80% yield; 45% is obtained on heating 1.39 g. I, 0.6 g. AcOH , and 1 ml. concd. HCl 2 hrs. at reflux; 45% also results from 1.39 g. I, 0.65 g. AcNH_2 , and 2.6 ml. concd. HCl after 2 hrs. at 120° in a sealed tube, while substitution of EtOAc for AcNH_2 gave 65%. Similarly, AcCl and *o*- EtNH - $\text{C}_6\text{H}_4\text{SH}$ (II) gave 72% 2-methylbenzothiazole-*EtI*, m. 191°, while *o*- PhCH_2NH - $\text{C}_6\text{H}_4\text{SH}$ (III) gave 65% 3-benzyl-2-methylbenzothiazolium iodide, m. 201°, and *o*- $\text{HOCH}_2\text{CH}_2\text{NH}$ - $\text{C}_6\text{H}_4\text{SH}$ gave 45% 3-carboxymethyl-2-methylbenzothiazolium iodide, m. 207° (decompn.; from EtOH). I (1.4 g.) and 1.1 g. EtCOCl in C_6H_6 gave 78% 2-ethylbenzothiazole-*MeI*, m. 175-5° (from H_2O), also obtained in 68% yield from I, EtCOEt , and concd. HCl in 4 hrs. at 120-40°; similarly, EtCOCl and II gave 70% 2-*n*-ethylbenzothiazolium iodide, m. 191°, while PrCOCl and I gave 75% 2-propylbenzothiazole-*MeI*, m. 215° (also obtained in 80% yield from I and PrCOEt in 5 hrs. at 120-40°). PrCOCl and II in C_6H_6 similarly gave 62% 3-ethyl-2-propylbenzothiazolium iodide, m. 181-2°, while AmCOCl and I gave 73% 2-amylbenzothiazole-*MeI*, m. 180° (from EtOH); $\text{C}_6\text{H}_5\text{COCl}$ gave 54% 2-heptylbenzothiazole-*MeI*, m. 169° (from EtOH - Et_2O), while $\text{C}_6\text{H}_5\text{COCl}$ gave 50% 2-nonylbenzothiazole-*MeI*, m. 232°, and $\text{C}_{11}\text{H}_7\text{COCl}$ gave 44% 2-undecylbenzothiazole-*MeI*, m. 217°, while III in the latter reaction gave 71% 3-benzyl-2-undecylbenzothiazolium iodide, m. 295°; chloride, m. 192-3°. I with $\text{C}_6\text{H}_5\text{COCl}$ in C_6H_6 gave 60% 2-phenylbenzothiazole-*MeI*, m. 330° (decompn.) (chloride intermediate, m. 289-90°, while II gave 50% of the corresponding ethiodide, decomp. 349° [the intermediate chloride, m. 265-7° (decompn.)], and III gave 3-benzyl-2-phenylbenzothiazolium chloride, m. 251° (decompn.; from EtOH), which gave 50% of the iodide, decomp. 286°; similarly $\text{C}_6\text{H}_5\text{COCl}$ and I in Et_2O gave 50% 2-heptylbenzothiazole-*MeI*, decomp. 323°, from the corresponding chloride, m. 261-2°, while III gave 45% benzyl-2-heptylbenzothiazolium iodide, decomp. 307°, from the corresponding chloride, m. 268° (decompn.). BrCl and I in C_6H_6 gave 81% 2-phenylbenzothiazole-*MeI*, yellow plates, m. 198°, while PhCH_2COCl gave 58% 2-benzylbenzothiazole-*MeI*, yellow needles, m. 190°. I and $\text{C}_6\text{H}_5\text{CH}_2\text{COCl}$ in cold PhMe gave 53% 1,2-bis-(2-benzothiazolyl)ethane-2-*MeI*, yellowish plates, m. 285-6°, which is poorly sol. in H_2O and with KI gave the dimethiodide, decomp. 310°, yielding with alkali a yellow base. Fumaryl chloride gave the dimethiodide of the ethylene analog, yellow needles, decomp. above 300°, which forms the dimethiodide, red brown, decomp. before melting; addn. of alkali to the chloride gave a yellow infusible solid which has 4 times the calcd. mol. wt. $\text{C}_{12}\text{H}_{10}\text{N}_2\text{S}_2$. Addn. of 1.39 g. I in 3 ml. C_6H_6 to 1.04 g. BrCH_2COCl in C_6H_6 and 0.5 hr.'s heating gave 30% 2-(bromo-methyl)benzothiazole-*MeI*, decomp. 197° (from H_2O), which is readily hydrolyzed by water and must be crystallized in the presence of H_2O . Cl_3CHCOCl in the above gave 30% 2-(trichloromethyl)benzothiazole-*MeI* (after the usual treatment with KI), decomp. 292-3° (from EtOH). Refluxing 1.39 g. I, 0.6 g. HCO_2H , and 1 ml. concd. HCl , followed by treatment of the ppt. with aq. KI , gave 10% benzothiazole-*MeI*, m. 211° (from EtOH).

G. M. Kondajoff

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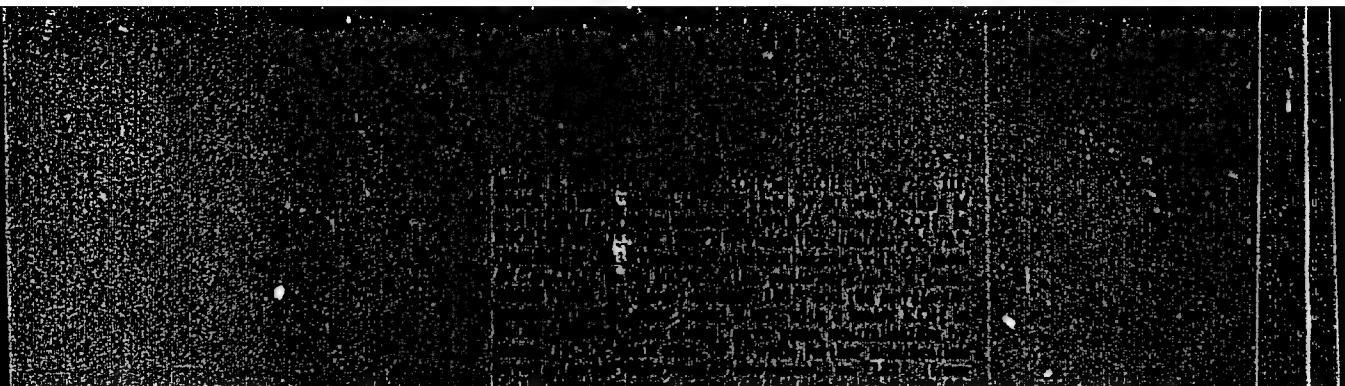


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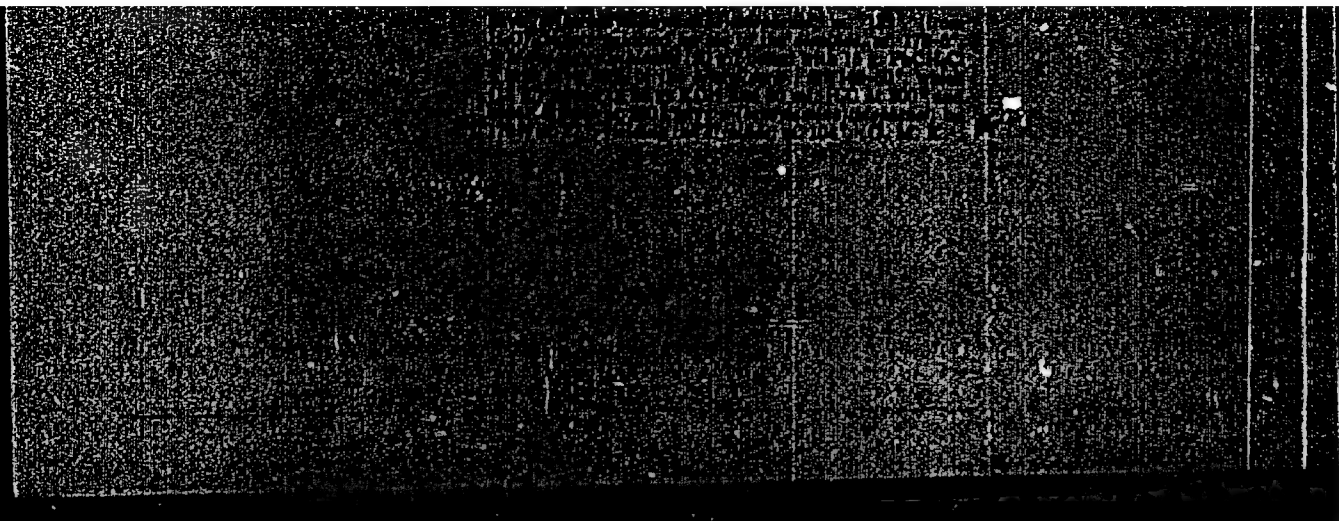


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N-Alkyl and N-aryl o-aminophenyl mercaptans. A. I.
Kiprianov and Z. N. Patenko. *J. Gen. Chem. U.S.S.R.*
19, 1329-35(1949)(Engl. translation).--See C.A. 44,
3487c. H. L. M.

1951

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Structure of Iodoline. A. I. Kuznetsov, B. Serdyukov, and V. P. Chernetskii. *Doklady Akad. Nauk S.S.S.R.* 66, 451 (1949); cf. *C.A.* 43, 4249c. Cherny and English (*C.A.* 43, 3037i) prep. 1,6- and 1,9-dimethoxyphenazines (*C.A.* numbering), but failed to prove definitely the precise configuration of their 2 products; the product m. 245.6° was identical with the reduction product of iodoline. This substance is now shown to be the 1,6-isomer, indicating the correct structure of iodoline. Condensation of 4-methoxy-*o*-quinone with 3,1,2-MeOC₆H₄(NH)₂ and separation of the products via their picrates, gave a substance m. 290° (picrate, m. 258°), and an isomeric dimethoxyphenazine, m. 251°, obtained from the mother liquor of the 1st isomer (C. and D. give m. 245.6°). Condensation of *o*-O₂N-C₆H₄OMe with *o*-anisidine in presence of powdered KOH gave the product m. 251°, identical with above described, proving it to be the 1,6-isomer. Hence, the dimethoxyphenazine, m. 290°, must be the 1,9-isomer. Further, condensation of *o*-O₂N-C₆H₄OMe with *m*-anisidine gave the 1,9-dimethoxyphenazine, m. 250.6°, identical with the above, and a dimethoxyphenazine, m. 174° (from ligroin), which must be the 1,7-isomer. G. M. Kosolapoff

(BA - A II Ja 53:115)

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Color and planarity of molecules of organic dyes. A. I. Kiprianov and I. K. Usenko. *Izv. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1990, 492-500; cf. C.A. 41, 8733g, 7837b. In org. dyes with NMe₂ as the auxochrome group, substituents in an ortho position to the NMe₂ group

which, through steric hindrance, enforce a rotation of that group relative to the plane of the ring, and thus disturb the planarity of the mol., give rise to a decrease of the absorption of light and to a shift of the absorption max. to shorter waves. Examples are *p*-(*p*-Me₂NC₆H₄N:NC₆H₄NO₂) and

p-(*p*-Me₂NC₆H₄NCI:Cl₂:NMe₂, both without and with Me in ortho-position to the NMe₂ groups. Similar changes, attributable to a perturbation of the planarity of the mol. as a result of substitution of H in the NH₂ group by 2Me, and the corresponding increase of the size of the group, were found in the recently synthesized cyanine dyes, ACH:CH:CH:B



(R = Me, Y = Me, Z = NH₂), which gives a blue soln in alc. (absorption max. 504 mμ) but which, after substitution of the H in the 2NH₂ groups by 2Me, has a max at 476 mμ and appears red-purple in alc. soln. Here, contrary to the usual effect of a methylation of the NH₂, the absorption shifts to shorter instead of to longer waves, and that as a result of the perturbation of planarity due to steric hindrance, coplanarity of the NMe₂ group with the ring having become impossible. Substitution of H atoms for the Me groups in the rings has no effect on the absorption, whereas in the compd. with NMe₂ instead of NH₂, that same substitution shifts the absorption max. by 33 mμ to longer waves. Changes in the position of the absorption max. are also produced when the coplanarity of the chromophore system, i.e. of the conjugated aromatic or heterocyclic rings, is disturbed by the substitution, as in the substituted monomethinecyanines of the type AC(R'):B(Y and Z are always H). Following are, for the different substituents R and R', the positions of the absorption max. (mμ) and the values 10⁻⁴ F of the absorption coeff.: H, H, 425, 8.0; Me, H, 425, 8.1; Et, H, 425, 7.8; Pr, H, 426, 7.3; Ph, H, 430, 7.5; H, Me, 426, —; H, Et, 425, —; H, Pr, 427, —; Me, Me, 448, 4.7; Et, Me, 480, 4.3; Me, Et, 446, 4.7, —; Me, Pr, 466, 4.8. Steric hindrance to coplanarity is present only in the last 4 deriva., and only these show a shift of absorption to longer waves and a lowering of F. The noncoplanarity of these 4 deriva. manifests itself also in the low yields, not over 15%, of their synthesis. The compd. 2,4,6-(NO₂)₃C₆H₂CH:CH:R (R = Me, Y = H, Z = H) in benzene soln. is red and has a max. of absorption

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with a closed polymethylene bridge of the type $\text{AC}(\text{CH}_2)_n\text{C}:\text{B}$ (Y and Z are always H) the color varies in a peculiar way with n ; the max. and 10^{-4} E are, for $n = 1$, 508, 14.8; $n = 2$, 601, 15.0; $n = 3$, 665, 13.0; $n = 4$, 573, 6.1. Is the styryl-type polymethylene dyo $p\text{-Me}_2\text{NC}_6\text{H}_4\text{CH}:\text{CHAr}$

(R = Me, Y = H, Z = H), easy substitution of the β -H given by an allyl gives rise to steric disturbance of the planarity, and in diene-iron complexes the max. to shorter waves, with a broadening of the intensity of absorption. The unsubstituted complex is at λ_{max} in red, max. Abs. mp. its β -Me deriv. is orange, max. 437 m μ . In all cases of disturbance of planarity, except in one, the intensity of the absorption is lowered. The position of the max. is always shifted to shorter waves when the noncoplanarity is brought about by forcing the mesochromic group out of the common plane; where the coplanarity of the rings themselves is disturbed, the max. can suffer a shift either to shorter or to longer waves. Noncoplanarity is further aided, with such properties as absence or near-absence of phosphorescence, lower melting temp., greater soft. in a.c., lower resistance to decoloration by acids, particularly alkali, and lower resistance to decoloration by light. N. Thorpe

KIPRIANOV, A. I.

CATALYST

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Dyes and Textile Chemistry

yellow
Synthesis of dyes from Michler's ketone and heterocycles containing an active methyl or methylene group.
O. M. Oksenrender and A. I. Kiprianov. *Ukrain. Khim. Zhur.* 16, 333-33 (1960) (in Russian).—Heating 1 g. 2-methylbenzothiazole and 1.07 g. Michler's ketone (I) in 4 ml. Ac₂O 3 hrs. at 135-40°, followed by addn. of Et₂O, gave 11% 2-[2,2-bis(p-dimethylaminophenyl)vinyl]benzothiazole methiodide, red, decomp. 232°, abs. max. 630 mμ (5.1 × 10⁴); the same dye formed in 28% yield from auramine and 2-methylbenzothiazole methyl methosulfate. I and 2-methyl-6-methoxybenzothiazole methyl methosulfate gave similarly 6% 2-[2,2-bis(p-dimethylaminophenyl)vinyl]-6-methoxybenzothiazole methiodide, m. 185°, abs. max. 635 mμ (4.7 × 10⁴). I and 2-methyl-8-naphthobenzothiazole methyl methosulfate gave 7% 2-[2,2-bis(p-dimethylaminophenyl)vinyl]-8-naphthobenzothiazole methiodide, violet, decomp. 215°, abs. max. 635 mμ (8.1 × 10⁴). I and 2-methyl-6-nitrobenzothiazole gave 15% 2-[2,2-bis(p-dimethylaminophenyl)vinyl]-6-nitrobenzothiazole, decomp. 212°, abs. max. 574 mμ (5 × 10⁴). Heating 0.87 g. 2,6-dimethylbenzothiazole methyl methosulfate with 0.8 g. auramine 1 hr. at 140°, followed by 2 hrs. at 140° after addn. of 4 ml. Ac₂O and 1 drop pyridine, gave 21% 2-[2,2-bis(p-dimethylaminophenyl)vinyl]-6-methylbenzothiazole methiodide, green, decomp. 195°, abs. max. 626 mμ (4.4 × 10⁴). With auramine and 2-methylbenzothiazole ethyl ethosulfate treated as above there was formed 13% 2-[2,2-bis(p-dimethylaminophenyl)vinyl]benzothiazole methiodide, red, decomp. 272°, abs. max. 636 mμ (5.1 × 10⁴). Auramine and 2-methyl-6-methoxybenzothiazole methyl methosulfate gave 43% 2-[2,2-bis(p-dimethylaminophenyl)vinyl]-6-methoxybenzothiazole methiodide, m. 185°, abs. max. 630 mμ (6 × 10⁴). Auramine and 2-methyl-6-nitrobenzothiazole methyl methosulfate gave 22% 2-[2,2-bis(p-dimethylaminophenyl)vinyl]-6-nitrobenzothiazole methiodide, m. 185°, abs. max. 574 mμ (5 × 10⁴).
color

methylaminophenyl vinyl) - 6 - phenylthioanisole methiodide, m. 170°, abs. max. 593 mμ (4.9×10^4). Auramine and 2,4-dimethyl-5-carbethoxythianazole methyl methosulfate gave 32% green 2-[2,3-bis(p-dimethylaminophenyl)vinyl]-6-methyl-5-carbethoxythianazole methiodide, decomp. 214°, abs. max. 626 mμ (8.7×10^4). Heating 0.57 g. Miescher's thioisotone (II) and 0.26 g. Me₂SO₄ in 4 ml. toluene 1 hr. at 115°, followed by distn. of toluene, soln. of the base II methyl methosulfate in 5 ml. pyridine, and heating this with 0.81 g. 2-methyl-6-acetamidobenzoic acid methyl methosulfate 45 min. at 100-115° gave about 30% 2-[2,3-bis(p-dimethylaminophenyl)vinyl]-6-acetamidobenzoic acid methiodide, decomp. 176°, abs. max. 535 mμ (8×10^4). The same dye was also formed either from auramine or I in Ac₂O, but contained less than the theoretical amt. of N. Similarly, II, Me₂SO₄, and 2-methylbenzoic acid methyl methosulfate gave 7% 2-[2,3-bis(p-dimethylaminophenyl)vinyl]benzoic acid methiodide, m. 183°, abs. max. 606 mμ (6.5×10^4). Use of quinaldine methyl methosulfate in the above prepn. gave 23% 2-[2,3-bis(p-dimethylaminophenyl)vinyl]quinaldine methiodide, green, decomp. 267°, abs. max. 636 mμ (4.3×10^4). Use of trimethylindolenine methiodide in the above prepn. gave similarly 7% 2-[2,3-bis(p-dimethylaminophenyl)vinyl]-3,3-dimethylindolenine methyl perchlorate (N₂Cl₂) used for final pptn. instead of the usual KI, black-blue, m. 207°, abs. max. 628 mμ (3×10^4). Heating 0.5 g. 2,4-dimethylthiazole with 0.8 g. Me₂SO₄ 2 hrs. at 100° followed by heating as above with 2 g. II methyl methosulfate in

pyridine gave 23% 2-[2,3-bis(p-dimethylaminophenyl)vinyl]-6-methylthiazole methiodide, orange-brown, m. 261°, abs. max. 475 mμ (3.5×10^4). Melting together 0.3 g. 2-hydroxythianaphthene-3-carboxylic acid with 0.42 g. auramine at 135-80° until Nil, evolution stopped, followed by 1.5 hrs. in vacuo, finally at 180° gave a mist. which diss. with AcPh, followed by EtOH gave 58% 2-[bis(p-dimethylaminophenyl)methylene]-3,3-dihydro-5-oxathianaphthene, red, m. 240°, abs. max. 530 and 468 mμ (1.76×10^4 and 1.9×10^4). Auramine (1.33 g.), 1 g. 1-phenyl-3-methyl-5-pyrazolone, and 1 ml. xylene after heating at 130-40° to expel NH₃, finally in vacuo 1 hr. gave 58% 4-[bis(p-dimethylaminophenyl)methylene]-1-phenyl-3-methyl-5-pyrazolone, red-brown, m. 266°, abs. max. 486 mμ (5.4×10^4). Similarly 0.2 g. 3-ethylrhodanine and 0.33 g. auramine gave 41% 5-[bis(p-dimethylaminophenyl)methylene]-3-ethylrhodanine, red-brown, m. 227°, abs. max. 490-500 mμ (5.4×10^4). Similarly 0.4 g. rhodanine and 0.8 g. auramine gave 28% 5-[bis(p-dimethylaminophenyl)methylene]rhodanine, red, m. 224°, abs. max. 470-80 mμ (3.1×10^4). 3-Allylrhodanine and auramine gave 67% red 5-[bis(p-dimethylaminophenyl)methylene]-3-allylrhodanine, m. 208°, abs. max. 480-500 mμ (3.3×10^4). Heating 2.7 g. auramine and 2 g. 2-amino-3-phenyl-4-thiazolidinone 10 min. at 170°, then 10 min. with 2 ml. xylene, gave 11% 6-[bis(p-dimethylaminophenyl)methylene]-2-amino-3-phenyl-4-thiazolidinone, m. 276°, yellow-orange, abs. max. below 430 mμ. In the above-described condensations the order of reactivity of the quaternary salts declines in the order: II, auramine, I.

G. M. Kosloski

CA

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Color of organic dyes and planarity of their molecules.
 1. A. I. Kiprianov and I. K. Ushenko (Acad. Sci. Ukrain. S.S.R., Kiev). *Zhur. Obshchei Khim.* (J. Gen. Chem.) 20, 134-41 (1951). Cyanine dyes containing proximal groups of large size display a shift of absorption max. toward the red end of the spectrum and a corresponding decrease of the intensity of absorption in comparison with unsubstituted derivs. The explanation probably lies in destruction of planarity of mole. with bulky groups, leading to closing-up the energy differences between ground and excited states (cf. Brooker, *et al.*, C.A. 42, 1126a). Reducing 2-methylbenzothiazole-Mel with 2-methylmercaptobenzothiazole-Me₂SO₃ and NaOAc in EtOH gave yellow bis(3-methyl-2-benzothiazole)monomethine ynone sulide, decomp. 251° (from EtOH), λ_{max} 422 m μ , ϵ_{max} 8.1 ($\times 10^4$). 2-Ethylbenzothiazole-Mel gave bis(3-methyl-2-benzothiazole)-4-methylmonomethine ynone sulide, orange, decomp. 217°, λ_{max} 405, ϵ_{max} 6.0. Heating C₁₂H₅(CO₂H)₂ and 2-methylmercaptobenzothiazole-p-Me₄ monomethine ynone sulide, decomp. 315°, λ_{max} 420, ϵ_{max} 7.5. Refluxing 1.2 g. 2-(methylmercaptobenzothiazole-p-Me₄)(SO₃Ph) 1 g. 2-ethylbenzothiazole-

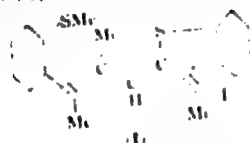
PhCl, and 1 g. NaOAc in EtOH gave bis(1-phenyl-2-benzothiazole)-4-methylmonomethine ynone sulide, decomp. 260°, benzene plates, λ_{max} 460, ϵ_{max} 3.8. Similar use of 2-propylbenzothiazole-Phl gave bis(3-phenyl-2-benzothiazole)-4-ethylmonomethine ynone sulide, m. 214° (from EtOH), λ_{max} 501, ϵ_{max} 2.1. Refluxing 0.78 g. 2-methylbenzothiazole-Phl and 1 g. 2-(2-acetamidovinyl)benzothiazole-Etl 15 min. in pyridine gave bis(3-ethyl-2-benzothiazole)(3-phenyl-2-benzothiazole)trimethine ynone sulide, decomp. 243° (from EtOH), green, λ_{max} 501, ϵ_{max} 11.8. Similarly, 2-ethylbenzothiazole-Etl and 2-(2-acetamidovinyl)benzothiazole-Phl gave bis(3-ethyl-2-benzothiazole)(3-phenyl-2-benzothiazole)-4-methylmonomethine ynone sulide, m. 158° (from EtOH), λ_{max} 502, ϵ_{max} 11.0, while 2-ethylbenzothiazole-Phl gave bis(3-ethyl-2-benzothiazole)-1-phenyl-2-benzothiazole-4-methylmonomethine ynone sulide, blue green, m. 252°, λ_{max} 570, ϵ_{max} 14.8, the corresponding Phl compd gave bis(3-phenyl-2-benzothiazole)-4-methylmonomethine ynone sulide, decomp. 275° (from EtOH), λ_{max} 572, ϵ_{max} 15.0.

over

while the mother liquor gave a *crystine* without Me on the methine chain, $C_{18}H_{14}N_4S_2$, m. 277°, λ_{max} 565. Re-fluxing 1 g. 2-(1-naphthylmethyl)benzothiazole-PhI, 1 g. $HC(OEt)_3$, and 1 ml. Ac_2O gave 35% *bis*(1-phenyl-2-benzothiazole)-8,10-di-1-naphthyltrimethineyanine perchlorate, lustrous crystals, decampg. 101.7° (from EtOH), λ_{max} 592, ϵ_{max} 9.5. 2-(2-Tetrahydronaphthylmethyl)benzothiazole-PhI and $HC(OEt)_3$ gave crude *bis*(1-phenyl-2-benzothiazole)-8,10-(tetrahydro-2-naphthyl)-trimethineyanine perchlorate, λ_{max} 580. Heating 2-ethylbenzothiazole-MeI and $HC(OEt)_3$ in pyridine gave *bis*(3-methyl-2-benzothiazole)-8,10-dimethyltrimethineyanine iodide, lustrous needles, decampg. 221°, λ_{max} 570, ϵ_{max} 7.0, while heating 3-benzylbenzothiazole-MeI with $HC(OEt)_3$ in Ac_2O gave 22% *bis*(3-methyl-2-benzothiazole)-8,10-diphenyltrimethineyanine perchlorate, violet, decampg. 152°, λ_{max} 580, ϵ_{max} 4.1; 2-(1-naphthylmethyl)benzothiazole-MeI gave 20% *bis*(1-methyl-2-benzothiazole)-8,10-di-1-naphthyltrimethineyanine perchlorate, violet, decampg. 170° (from EtOH), λ_{max} 568, ϵ_{max} 3.7, and the tetrahydro-2-naphthyl analog yielded *bis*(3-ethyl-2-benzothiazole)-8,10-bis(tetrahydro-2-naphthyl)trimethineyanine perchlorate, 25%, blue, decampg. 152° (from dil. EtOH), λ_{max} 578, ϵ_{max} 2.1. Chloromethylation of tetrahydronaphthalene gave 52% (3-chloromethyl) deriv, bp 130-42°; this (71 g.) boiled 3 hrs. with 20 g. KCN in 400 ml. EtOH and 70 H₂O gave the nitrile (72%), bp 178-82°, which boiled 10 hrs. with 30% NaOH gave 70% tetrahydro-2-naphthalene-1-carboxylic acid, m. 83° (from H₂O); amide, m. 142° (from H₂O), was a by-product. The free acid and NaCl₂ gave 78% of the acyl chloride, bp 143-4°, which with *o*-Me-NHC₆H₄SO₃H in C₆H₆ gave a yellow mass yielding on soln in H₂O and addn. of K₂Cr₂O₇ 2-(tetrahydro-2-naphthylmethyl)-benzothiazole-MeI, m. 220° (from H₂O). The results of Ushenko (Ukrain. Khim. Zhur. 14, 50 (1948)) are interpreted similarly to the above. (G. M. Kosolapoff)

CA

Reaction of methylene derivatives of the thiazole series with alkyl halides. A. I. Kiptanov and P. S. Rubchev (State Univ., Kiev). *Zh. obshch. Khim.* (U.S.S.R. Chem.) 20, 146-57 (1950). Methylene-derivs. of thiazoles generally form with alkyl halides a 2:1 adduct, which is easily hydrolyzed. Mel (21 g) and 22 g 3-methyl-2-methylenebenzothiazoline (m. 104-6°) in 50 ml. CHCl₃ gave 95% yellow adduct, needles, m. 220-30°, probably based on the dimer of the thiazoline and having the probable structure (I); other solvents give the same product.



although in EtOH the product is obtained in impure

state; heating I with 1:10 HCl gave 3-methyl-2-(acetyl-methylene)benzothiazoline-HCl (free base, m. 157-8° on crystn. from EtOH, m. 160-1°), while the mother liquor after addn. of NaOH gave 87% o-methylmercapto-N-methylbenzothiazoline, b.p. 120-8°; 1:10 HCl, m. 161°; 1:10 AcOH, m. 161°. Similar reaction with EtI gave the Et analog of I, m. 160-1°, which heated with 1:10 HCl gave 91% of the same thiazoline-HCl deriv. (above) and 73% o-methylmercapto-N-methylbenzothiazoline, b.p. 112-14° (Ac deriv., m. 55° from petr. ether). Similar reaction of Mel with 3-ethyl-2-methylenebenzothiazoline gave 92% 3-Et analog of I, m. 192-3° (from EtOH), which heated with 1:10 HCl gave 84% 3-ethyl-2-(acetyl-methylene)benzothiazoline, m. 115-16°, and o-methylmercapto-N-ethylbenzothiazoline, b.p. 99-101° (Ac deriv., m. 66-7°). Similar reaction of 3-methyl-2-methylene-o-naphthothiazoline (from 2-methyl-o-naphthothiazole-MeSO₂, m.p. close to dimeric) with Mel in warm CHCl₃ gave 67% corresponding analog of I, m. 270-7° (from pyridine), this heated 5 min. with aq. alk. NaOH gave 79% 3-methyl-2-methylmercapto-N-methylbenzothiazoline, m. 202-3°, and 66% 3-methylmercapto-2-methylbenzothiazoline, m. 167° (from EtOH). 1:10 AcOH, m. 157° (from EtOH). 1:10 gave 92% corresponding analog of I, m. 246-7° (above).

compd 1, which on hydrolysis with dil. alk. NaOH gave the same 1-methyl-2-(acetylmethylene)-6-naphthothiazoline and 52% 1-ethylmercapto-2-(naphthylamino)naphthol-6-ol 1,4-deriv., m. 112-113° from petr. ether). 2-Methyl-4,5-diphenyl-2-methylene-thiazoline (propd. in 91% yield analogously from the corresponding methosulfate, m. 152-153° (decompn.), is nearly dimeric (in C₆H₆); its reaction with MeI gave the corresponding analog of 1, decompn. 183-184° (from EtOH), which heated with dil. alk. HCl gave PhCH(SMe)Ph, m. 75-76° (from EtOH) (with PhNH₂ yields [PhC(SNH₂)Ph]₂ MeNH₂ (identified as the HCl salt, m. 226-6°), and 80% 3-methyl-4,5-diphenyl-2-(acetylmethylene)thiazoline, m. 220-20° (from EtOH), which yields cyanine dyes on warming with quaternary salts of N heterocycles. R11 in the above reaction gave 93% of the corresponding analog of 1, decompn. 214-15°, which on hydrolysis in dil. alk. HCl gave 75% thiazoline deriv. (above) and 83% PhCH(SMe)Ph, m. 78° (also yielding a benzil deriv. with PhNH₂). 3-Methyl-6-nitro-2-methylenebenzothiazoline (by similar reaction of the corresponding methosulfate, m. 73° yield, decompn. 240-2°, dimeric mol. wt. 1) on heating 1.5 hr. in a sealed tube with MeI gave only 2-methyl-6-nitrobenzothiazole-MeI, similar reaction at 180° with Me₂SO, gave only the corresponding Me methosulfate, m. 211-4°.

G. M. Kovalev

KIPRIANOV, A. II

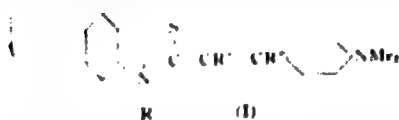
Kiprianov, A. I. & Babichev, F. S. - "Investigation in the field of hydroxy-fuchsone dyes. X. On the so-called tautomerism of hydroxy-triaryl-carbinols." (p. 158)

SO: Journal of General Chemistry, (Zhurnal Obshchei Khimii), 1950, Vol. 20, No. 1

10

CA

"Color of organic dyes and the planarity of their molecules. II. A. I. Kiprianov and I. K. Uschenko (Acad. Sci. Ukr. S.S.S.R.), *Zhur. Obshch. Khim.* (J. Gen. Chem.) **20**, 511-17 (1950); cf. *Chim.* **44**, 573g. — The absorption spectra of the several styryl dyes, studied show a displacement of the max. to the shorter waves with concurrent decrease of intensity when alkyl or aryl groups are substituted in the α or β positions of the fundamental unit (I). The results are explained by destruction of co-



planar structure of the benzene and the thiazole rings. The following max. (m μ) and ϵ were observed (R, R', R'' given): Ph, H, H (I), 500, 6.2×10^4 ; Ph, Me, H (II),

500, 2.4×10^4 ; Ph, H, H (III), 500, 2.6×10^4 ; Ph, H (IV), 500, 3.4×10^4 ; Et, H, H (V), 500, 1.1×10^4 ; Et, Me, H (VI), 481, 6.2×10^4 ; Et, Et, H (VII), 482, 1.1; Ph, H (VIII), 488, 2.5×10^4 ; Ph, H, Me (IX), 552, 2.2×10^4 ; Ph, H, Ph (X), 550, 1.5×10^4 ; Et, H, Me (XI), 510, 2.1×10^4 , resp. New syntheses were as follows: VI was prepd. in 50% yield by refluxing 1 hr. 0.5 g. 2-ethylbenzothiazole-4-yl, 0.4 g. p-MeNC₆H₄CH₃ (I), and 2 ml. Ac₂O, followed by addn. of NaClO₄ in EtOH, yielding the *eth-perchlorate* in 20% (decomp. from EtOH). VII, prepd. similarly could not be obtained completely pure. VIII was prepd. similarly from 2-benzylbenzothiazole-4-yl and isolated as the *eth-perchlorate*, decomp. 172°, cherry-red, in 18% yield. IX prepd. similarly from 2-methylbenzothiazole-4-yl and p-MeNC₆H₄CH₃ in 20% yield, isolated as the *phenyl perchlorate*, decomp. 215° (from EtOH). X in 16% yield, similarly prepd. from p-MeNC₆H₄CH₃, decomp. 205° (from EtOH). XI, isolated as the *eth-perchlorate*, decomp. 201° red, obtained in 31% yield from 2-methylbenzothiazole, p-MeC₆H₄SO₂Et, and MeNC₆H₄CH₃ in Ac₂O. G. M. K.

10

CA

The color of organic dyes and the planarity of their
molecules. H. A. I. Kiprianov and I. K. Ushenko
Dokl. Akad. Nauk S.S.S.R. 20, 843 (1958) (Engl. translation)
Sov. Chem. 44, 7617b. R. M. S.

1951

KIPRIANOV, A.I.

"Iodine Synthesis," Dkk. AN., 70, Nol 4, 1950. Inst. of Org. Chem., Ukrainian SSR
Acad. Sci., -c1950-.

KIPRIANOV A. I.

Nov 50

USSR/Chemistry - Photographic
Sensitizers

"Cyanin Dyes Containing Fluorine. I. Cyanin
Dyes From Derivatives of 6-Fluorobenzothiazol,"
A. I. Kiprianov, L. M. Yagupol'skiy, Chair of
Org Chem, Kiev State U

"Zhur Obshch Khim" Vol XX, No 11, pp 2111-2117

Synthesized 2-methyl-6-fluoro- and 2-methyl-
mercapto-6-fluorobenzothiazols and their
quaternary salts. Obtained 11 thiocyanin
dyes containing F as substitute in position 6,

170728

Nov 50

USSR/Chemistry - Photographic
Sensitizers (Contd)

in place of H. Showed this substitution has
practically no effect on position of maximum
absorption, as distinguished from Cl, Br, and
I.

170728

OKSENGENDIER, G.M.; KIPRIANOV, A.I.

Condensation of auramine with 2-aminothiazole derivatives. Ukr.khim.shur.
17 no.5:736-743 '51. (MLRA 9:9)

1. Institut organicheskoy khimii AN USSR.
(Auramine) (Thiazole)

OKSENGENDLER, G.M.; KIPRIANOV, A.I.

Condensation of β, β -bis(*p*-dimethylaminophenyl)-acrolein with heterocyclic compounds containing an active methyl or methylene group. Ukr.khim.shur.17 no.5:744-750 '51. (MLRA 9:9)

1. Institut organicheskoy khimii AN USSR.
(Acrolein) (Dyes and dyeing--Chemistry)

KIPRIANOV, A. I.

Pa. 173736

USSR/Chemistry - Photographic Sensitizers Jan 51

"Investigation Into Series of Derivatives of Benzo-1,4-thiazine. I. Quaternary Salts of Benzo-1,4-thiazine and Its Derivatives," A. I. Kiprianov, Z. N. Puzenko, Inst Org Chem, Acad Sci Ukrainian SSR

"Zhur Obshch Khim" Vol XII, No 1, pp 156-163

Synthesized heretofore unknown quaternary salts of benzo-1,4-thiazine deriv by condensing 4-halo-phenols with N-ethyl- or N-aryl-o-aminophenols. Obtained 6 methyl- and phenylperchlorates of benzo-1,4-thiazine. Synthesized methylperchlorate of benzo-1,4-thiazine by condensing

173736

USSR/Chemistry - Photographic Sensitizers Jan 51
(Contd)

N-methyl-o-aminophenol with sym dibromethylene. Shown that above salts are easily isomerized into their quaternary salts of 2-allylbisbenzothiazols.

173736

KIPRIANOV, A., I.,

Pa. 173138

USSR/Chemistry - Photographic Sensitizers Jan 51

"Investigation Into Series of Derivatives of Benzo-1,4-thiazine. II. Cyanine Dyes of Benzo-1,4-thiazine Series," A. I. Kiprianov and Z. N. Pazenko, Izv. Akad. Nauk SSSR, Ser. Khim., 1950, No. 1, pp. 163-170

"Zhur. Obshch. Khim." Vol. XXI, No. 1, pp. 163-170

Describes 9 new cyanine dyestuffs (benzo-1,4-thiazinocyanines). Synthesized them (2 monomethine-, 6 trimethine-, and 1 pentamethinecyanine) by heating quaternary salts of benzo-1,4-thiazine and its

USSR/Chemistry - Photographic Sensitizers Jan 51
(Contd.)

deriv with orthoformic ester in pyridine or in mixt of acetic anhydride and pyridine. Due to isomerization thiacarboxyanines formed simultaneously with thiazinocarboxyanines.

173137

KIPRIANOV, A. I.

Pa. 173138

USSR/Chemistry - Photographic Sensitizers Jan 51

"Investigation Into Series of Derivatives of Benzo-1, 4-Thiazine. III. Condensation of Quaternary Salts of Benzo-1, 4-Thiazine and Its Derivatives With Aldehydes," A. I. Kiprianov, A. M. Pavlenko, Inst Org Chem, Acad Sci Ukrainian SSR

"Zhur Obshch Khim" Vol XXI, No 1, pp 170-174

Condensed quaternary salts of 3-methylbenzo-1, 4-thiazine and certain deriv with p-dimethyl-sulfobenzaldehyde in acetic anhydride to form car stylys, which are unstable to action of

173138

USSR/Chemistry - Photographic Sensitizers Jan 51
(contd)

allalls. Quaternary salts of benzo-1, 4-thiazine and deriv not contg methyl group in 3 position condensed with aromatic aldehydes at methylene group in 2 position of thiazine ring.

173138

KIRILIANOV A. I.

PA 194T51

USSR/Chemistry - Thiocyanine Dyes and Nov 51
Benzothiazole Derivatives

"Ultraviolet Absorption Spectra of Benzothiazole Derivatives," A. I. Kiril'yanov, Yu. S. Rozum, Inst of Org Chem, Acad Sci USSR

"Zhur Obshch Khim" Vol XXI, No 11, pp 2038-2045

Studied ultraviolet absorption spectra in alc solns of 2-methylbenzothiazole (I), its derivs contg amino groups on benzene rings, 2-ethyl- α -naphthothiazole, and a number of quaternary salts of benzothiazole derivs. Detd absorption curves of 2 methylene bases formed under action

194T51

USSR/Chemistry - Thiocyanine Dyes and Nov 51
(Contd)

of Na alcoholate on alk soln of iodomethylates of I and 2-methyl-6-dimethylaminobenzothiazole (II) and of II with different concns of H_2SO_4 in soln. Absorption curves of II in alc soln at increasing concns of H_2SO_4 showed that salt of this base forms much more easily on amino group than on benzothiazole ring.

194T51

KRAVCHENKO, V.M.; PASTUKHOVA, I.S.; KIPRIANOV, A.I., diyenny chlen.

Indol in binary systems binuclear compounds. Dop.AN URSS no.3:193-200 '52.
(MLRA 6:9)

1. Akademiya nauk Ukrayins'koyi RSR (for Kiprianov). 2. Donets'kyi industrial'-
nyy instytut im. M.S.Khrushchova (for Kravchenko and Pastukhova).
(Indol)

HORBAN', A.K.; KIPRIANOV, A.I., diysnyy chlen.

Acetaldehyde alkyl- β -chloroethyl acetals. Dop.AN URSS no.3:201-204 '52.
(MIRA 6:9)

1. Akademiya nauk Ukrayins'koyi RSR (for Kiprianov). (Acetals)

HORBAN', A.K.; KIPRIANOV, A.I., diysnyy ohlen.

Action of an alcoholic solution of alkali on β -chloroethyl acetals of acetaldehydes. Dop.AN URSSR no.3:205-207 '52. (MLRA 6:9)

1. Akademiya nauk Ukrayins'koyi RSR (for Kiprianov). (Acetals)

1. KIPRYANOV, A.I.
2. USSR (600)
4. Chemistry, Organic
7. The second conference of the Ukrainian republic on organic chemistry, Ukr.khim.zhur. 18 no. 1, 1952.
9. Monthly List of Russian Accessions, Library of Congress, ..PRIL 1953, Uncl.

KIPRIANOV, A. I.; PAZENKO, Z. I.

"Scientific Records of the A.M. Gor'kii State University in Kharkov. Vol. 38.
Transactions of the Scientific Research Chemical Institute. Vol. 9" Reviewed by
A. I. Kiprianov, Z. N. Pazenko, Ukr. khim. zhur, 18 no. 3:335-336 '52.
(MIRA 6:0)

Institut organicheskoy khimii Akademii nauk Ukrainskoy SSR.
(Chemistry--Periodicals)

KIPRIANOV, A.I.

Color of organic compounds and the so-called resonance theory. A.I. Kiprianov. *Ukrain. Khim. Zh.* 18, 989-99 (1962). The resonance point of view in explanation of color phenomena is criticized on grounds of idealism and the author's previous work on color is presented. It is suggested that the formulation of substances in which "resonance" exists in conjugated systems, be written with an outline of dots around the formula to indicate equalization between single and double bonds; in cases of incomplete equalization a long broken arrow outline around the affected parts of the mol. is suggested. O. M. Kosholov

KIPRIANOV, A. I.

Effect of the solvent on color of organic coloring substances. III. A. I. Kiprianov and M. R. Pashchenko (Kiev State Univ., Ukrain. Khim. Zvezd. 19, 341-37 (1952); *Chem. Abstr.* 47, 8475d); preceding abstract. A series of dyes was prepd. by condensation of quaternary salts of N-heterocycles with active Me groups, with various aromatic aldehydes; the resulting products also were color in various neutral solvents. The color changes with change in polarity of solvents is discussed on the basis of changes in polarization of the dye molecules. Refluxing 1.2 g. 2,4-dimethylthiazole methyl methosulfate with 0.80 g. 2-hydroxy-1-naphthaldehyde in EtOH in the presence of a little piperidine 30 min. gave on cooling 21% red-brown (3,4-dimethyl-2,3-dihydro-2-benzothiazolidene) (1',3'-naphthoquinone) decomp. 225-7° (from EtOH), giving pink acid. in H₂O, red-violet in EtOH and violet in CHCl₃; abs.

max. in EtOH 572 mμ, in CHCl₃ or C₆H₆ 590. Similarly 3,4-dimethylthiazole methiodide and 1,4-hydroxynaphthaldehyde gave 31% (3,4-dimethyl-2,3-dihydro-2-benzothiazolidene) (1',3'-naphthoquinone) decomp. 213-19° (from EtOH) in presence of Ni(OH)₂, abs. max. in H₂O 500, in EtOH 594; in CHCl₃ 592; in C₆H₆ 574. 2-Methylbenzothiazole methiodide and 2-hydroxynaphthaldehyde similarly gave (3-methyl-2,3-dihydro-2-benzothiazolidene) (1',3'-naphthoquinone) decomp. 210-12° (from EtOH), abs. max. in EtOH 578, in CHCl₃ 590, in C₆H₆ 583. 2-Methylbenzothiazole methiodide and 4-hydroxynaphthaldehyde gave 18% (3-methyl-2,3-dihydro-2-benzothiazolidene) (1',3'-naphthoquinone) decomp. 243-9° (from EtOH); abs. max. in EtOH 567 in CHCl₃ 545, in C₆H₆ 532. Refluxing 1 g. 2-methyl-1-naphthothiazole methiodide with 0.38 g. salicylaldehyde in 5 ml. pyridine 30 min. gave a yellow ppt. (57%) of (3-methyl-2,3-dihydro-2-naphtho-2-thiazolidene) (6-quinone) decomp. 205°; this treated with aq. Ni(OH)₂ gave the base (anhydro form of the dye, C₁₇H₁₁ONS), violet, decomp. 178° (from EtOH) in presence of Ni(OH)₂, abs. max. in EtOH 562, in CHCl₃ 505. Similarly p-HOCH₂CHO gave 65% (3-methyl-2,3-dihydro-2-naphtho-2-thiazolidene) (6-quinone) decomp. 270°, which with aq. Ni(OH)₂ gave the base, violet, decomp. 180° (from EtOH).

OVER

A. I. KIPRIANOV

2/2

1. *2-hydroxy-1-naphthaldehyde* gave 85% (3-methyl-2,2-dihydro-2-naphtho-5-thiazolide) (1'-2'-naphthoquinone) in EtOH (decomp. 220-27° (from EtOH)), abs. max. in EtOH 591, in CHCl₃ 608, in C₆H₆ 606. Similar reaction of 2-methyl-2-naphthothiazole with 1-hydroxy-4-naphthaldehyde in EtOH (piperidine) gave 85% (3-methyl-2,2-dihydro-2-naphtho-5-thiazolide) (1'-2'-naphthoquinone) in EtOH (decomp. 225-30° (from piperidine)), abs. max. in EtOH 614, in CHCl₃ 638, in C₆H₆ 606. Reaction of 2-methyl-2-naphthothiazole with 1-hydroxy-4-naphthaldehyde in EtOH in presence of piperidine 1 hr. gave 85% orange (3-methyl-2,2-dihydro-2-naphtho-5-thiazolide) (1'-2'-naphthoquinone-HI; decomp. 222-3° (from EtOH)), with aq. NH₄OH this gave the free base, light blue, decomp. 144-7° (from EtOH), abs. max. in EtOH 583, in CHCl₃ 606, in C₆H₆ 606. Refusing 2-naphthothiazole methiodide and 1-hydroxybenzaldehyde in pyridine 1 hr. gave 46% orange (3-methyl-2,2-dihydro-2-naphtho-5-thiazolide) (1'-2'-naphthoquinone-HI; decomp. 234° (from EtOH)), abs. max. in EtOH 601, in CHCl₃ 638, in C₆H₆ 670, was found in the free base, brown, decomp. 200-10°, obtained by treatment of the above with NH₄OH. Similar reaction of 2-hydroxy-1-naphthaldehyde run in EtOH in presence of piperidine gave 80% (3-methyl-2,2-dihydro-2-naphtho-5-thiazolide) (1'-2'-naphthoquinone) in EtOH (decomp. 198-200° (from EtOH)), abs. max. in EtOH 594, in CHCl₃ 606, in C₆H₆ 600. Reaction of 2-methyl-2-naphthothiazole with 1-hydroxy-4-naphthaldehyde gave 100% (3-methyl-2,2-dihydro-2-naphtho-5-thiazolide) (1'-2'-naphthoquinone) in EtOH (decomp. 215° (from EtOH)), abs. max. in EtOH 616, in CHCl₃ 638, in C₆H₆ 602. 2-Methylpyridine methiodide and 1-hydroxy-4-naphthaldehyde in EtOH (piperidine) gave 42% brown ppt., which treated with aq. NaOH gave 35% (1-methyl-2,2-dihydro-2-pyridylidene-1'-2'-naphthoquinone) in EtOH (decomp. 180-10° (from EtOH)), blue-violet after vacuum drying, and green after drying at 100°, abs. max. in EtOH 430, in CHCl₃ 578, in C₆H₆ 584. Quinoline methiodide similarly gave 25% (1-methyl-2,2-dihydro-2-pyridylidene-1'-2'-naphthoquinone) in EtOH (decomp. 134-5° (from EtOH-NH₄)), abs. max. in EtOH 548, in EtOH 568, in CHCl₃ 608, in C₆H₆ 600. Similarly 2-methyl-2-phenylthiazole methiodide gave (3-methyl-2,2-dihydro-2-phenylthiazolide) (1'-2'-naphthoquinone) in EtOH (decomp. 220° (from EtOH)), abs. max. in EtOH 568, in CHCl₃ 601, in C₆H₆ 572; the ppt. formed directly from the reaction mixture gives red color in EtOH, turning yellow on addition of acids or blue with alkali; it appears to be a complex of quinhydrone type between the base and the HI salt. Similarly 2-methyl-4,6-diphenylthiazole methiodide gave 81% (3-methyl-2,2-dihydro-2,2-diphenyl-2-thiazolide) (1'-2'-naphthoquinone) in EtOH (decomp. 197-8° (from EtOH)), abs. max. in EtOH 618, in CHCl₃ 610, in C₆H₆ 594. 2,2,3-trimethylindolenine methiodide gave 64% (1,2,3-trimethyl-2,2-dihydro-2-indolenine) (1'-2'-naphthoquinone) in EtOH (decomp. 125° (from EtOH)), violet, abs. max. in EtOH 587, in CHCl₃ 630, in C₆H₆ 604.

G. M. Koshchepov

USSR/Chemistry - Benzothiazole Derivatives Feb 52

"Derivatives of Dibenzothiazolymethane," A. I. Kiprianov, L. P. Yakovlev, Yu. S. Rozum, Inst of Org Chem, Acad Sci Ukrainian SSR

"Zhur Obshch Khim" Vol XII, No 2, pp 302-309

Condensation of o-aminothiophenol with esters of methyl-, ethyl-, n-propyl-, iso-propyl-, phenyl-, and dimethylmalonic acids yielded 6 new bases: dibenzothiazolymethanes substituted in methane residue. Data ultraviolet absorption curves of dibenzothiazolymethane (I) and its 6 derivatives, compared them with absorption curves of 2-(N-methyl-benzothiazolylidene-(2))-methylbenzothiazole. Shown 209T28

USSR/Chemistry - Benzothiazole Derivatives Feb 52
(Contd)

that I and its mono derives develop tautomerism in solns. Prepd 3 new monomethinebenzothiazolines containing allyl as substituent at central C atom. Data their absorption curves in alc solns and showed that mols of these dyes exhibit spatial hindrances preventing coplanarity of thiazole rings.

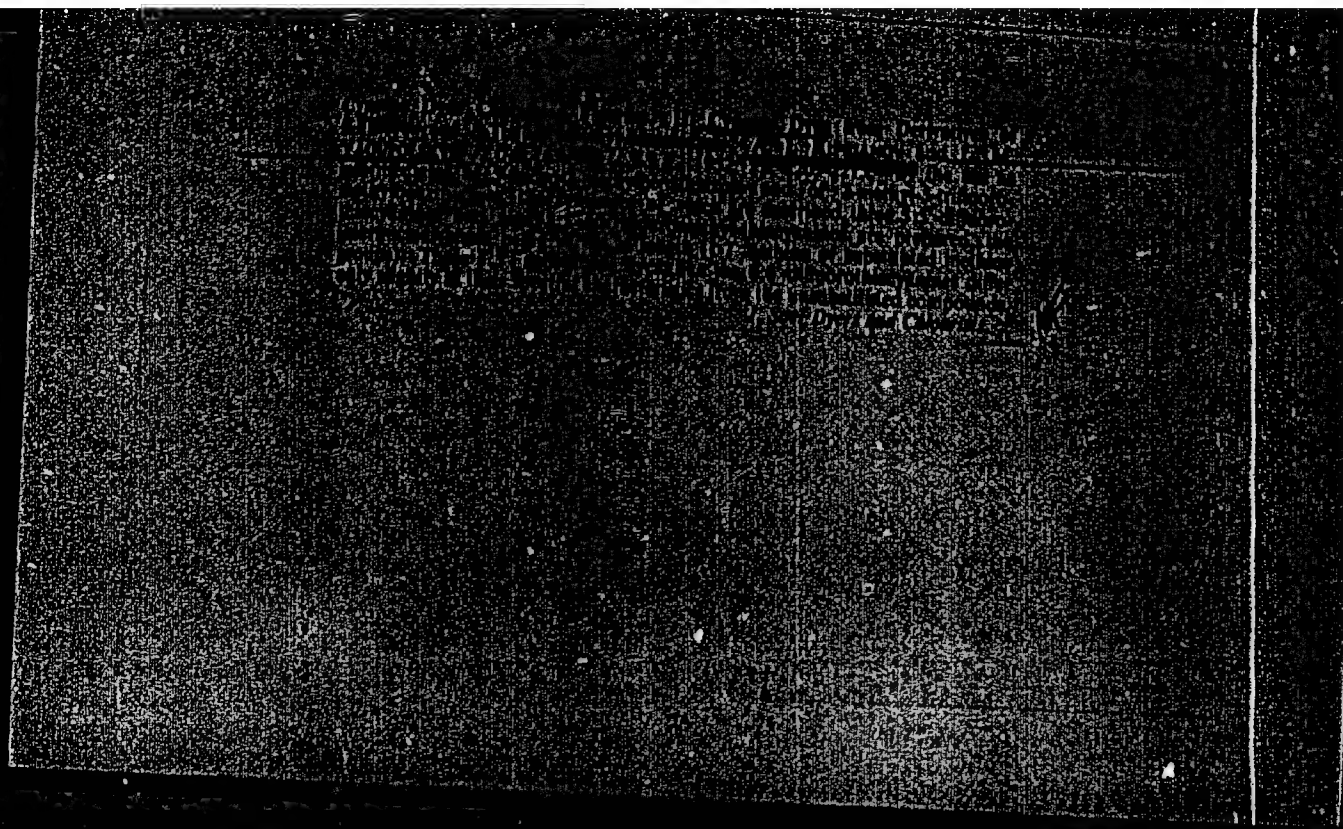
209T28

KIPRIANOV, A. I.

1. CHERNETSKIY, V. P., KIPRYANOV, A. I.
2. USSR (600)
4. Phenazines
7. Synthesis of N-oxides of phenazine derivatives. Part 1. Nono-N-oxides of alkoxyphenazines. Zhur. ob. khim., 22, no. 10, 1952
9. Monthly List of Russian Accessions, Library of Congress, February 1953. Unclassified.

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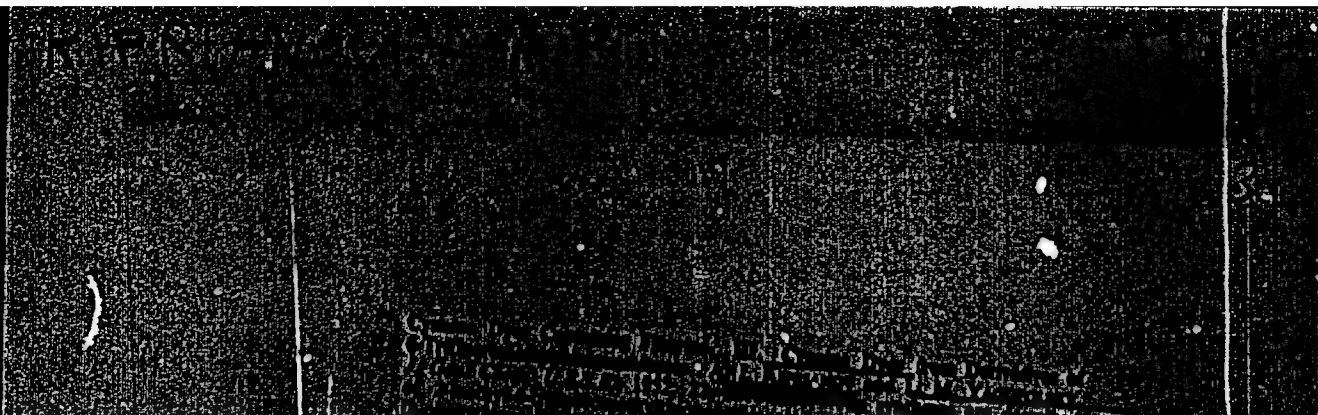


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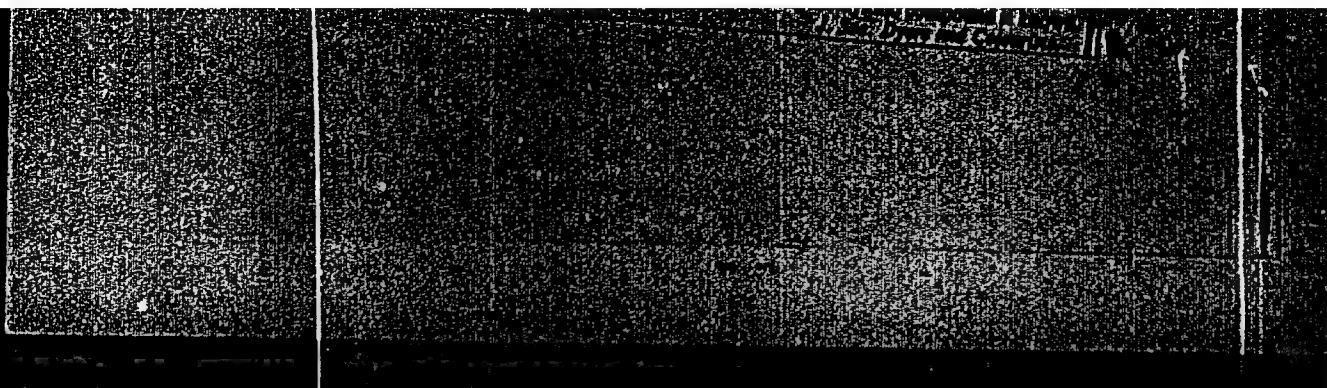


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KIPRIANOV, A. I.

PA 22/T10

USSR/Chemistry - Dyestuffs

1 Aug 52

"Coplanarity of Dimethylamino Group With the Benzene Ring and Its Auxochromic Action," A.I. Kiprianov, Acting Mem Acad Sci Ukrainian SSR I.N. Znamova, Inst of Org Chem, Acad Sci Ukrainian SSR

"Dok Ak Nauk SSSR" Vol 85, No 4, pp 789-791

Cyanine dyestuffs containing radicals in the ortho position to the amino group were studied. The amino group itself strongly shifts the absorption max to the long-wave region. Introduction of a methyl or ter-butyl group in the ortho position has little effect, but a dimethylamino group

22/T10

shifts absorption max by 33 m μ into the short-wave region. The dimethylamino group alone lowers the extinction max sharply, but introduction of a methyl or ter-butyl group into the ortho position results in a growth in extinction with a shift of the absorption max to the short-wave region. Thus the voluminous hydrocarbon radicals cancel the effect of dimethylamino groups on the color of dyestuffs.

(CA 47 no. 9:9979 (3)

22/T10

KIPRIANOV, A.I.; STOLIAROV, N.Z.

2-benzothiazolylacrylic acid and its derivatives. Ukr.khim.zhur.
19 no.1:57-60 '53. (MLRA 7:4)

1. Kiyevskiy gosudarstvennyy universitet im. T.G.Shevchenko, kafedra
organicheskoy khimii. (Acrylic acid)

KIPRIANOV, A.I.; KROSHCHENKO, M.M.

Synthesis of 1,2-benzophenazine derivatives. Ukr.khim.zhur. 19
no.1:73-80 '53. (MLRA 7:4)

1. Institut organicheskoy khimii Akademii nauk USSR.
(Phenazine)

KIPRIANOV, A.I.; POCHINOK, V.Ya.

2-aminomethylbenzothiazole. Ukr.khim.shur. 19 no.2:165-168 '53.
(MLRA 7:4)

1. Kiyevskiy gosudarstvennyy universitet, kafedra organicheskoy
khimii. (Thiazole)

KIPRIANOV, A. I.

USSR.

✓ Achievements of organic chemistry in fighting tuber-
culosis. A. I. Kiprianov. Ukrain. Khim. Zhur. 10, 230-
40 (1965). *Russk. Zhur. Khim.* 1964, No. 22634. —A
review. B. Wierbicki

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[illegible]

KIPRIANOV, A.I.

"Organic chemistry." E.C.Khotyns'ki. Reviewed by A.I. Kypryanov.
Ukr.khim.zhur. 19 no.4:461-462 '53. (MLRA 8:2)
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... from 2-methyl-4-methylthiazole.
A. I. Kiprianov and A. V. Gutsenko, *Ukrain. Khim. Zhur.*
1984, No. 19830.
2-methyl-4-methylthiazole (I) and 2-methyl-4-methylthio-
quinazolin-5(1H)-one (II) were synthesized in order to
obtain a dye containing a quinone residue in its mol. I and II are
weak bases forming no quaternary salts with dialkyl sulfates

